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Appendices A and B

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PERFORMANCE EVALUATION OF FULL-SCALE HAZARDOUS WASTE INCINERATORS

VOLUME III

APPENDICES A AND B

by

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16. ABSTRACT

This report is Volume III, Appendicies A and B, of a series of extensive performance data EPA obtained through eight (8) field tests of actual industrial/commercial incinerators, was prepared in response to the Agency's need to conduct a regulatory impact analysis (RIA) for hazardous waste incinerators to determine the need, adequacy, and economic feasibility of current RCRA incinerator regulations. Tests involved trial burn-type testing at each plant during typical albeit closely monitored daily operations on wastes typical of their routine disposal function.

Most incinerators were found to be closely approaching or performing within RCRA requirements for destruction of compounds, although some facilities showed substandard results in other areas.

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory-Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report is one of a five-volume series of reports presenting the recent testing and evaluation results of the performance of eight (8) commercial and industrial hazardous waste incinerators. The Agency's purpose was to gather accurate data on full-scale incinerator environmental performance, for the EPA's use in developing a regulatory impact analysis document in the near future for all such incinerators subject to existing RCRA standards. Because the performance information contained herein is of high interest to the hazardous waste incineration technical community in general, EPA wishes to make it available as a technical report at this time.

The material contained in this report has been reviewed and approved by experts within the Agency with state-of-the-art knowledge of the operation, testing, and evaluation of incinerator performance. During sampling and analysis of the incinerators in the field, EPA's most modern and scientific methods were employed along with the appropriate level of quality assurance and quality control. The incinerators were studied during a closely monitored mode of operation while disposing of mixtures of real-world hazardous wastes typical of their usual feedstocks. We are pleased to report that under these circumstances the incinerators were generally successful in performing their task of safely destroying hazardous waste and controlling other harmful emissions to the environment with some exceptions.

Requests for further information regarding this report on performance of full-scale incineration facilities should be directed to the Energy Pollution Control Division, IERL, Cincinnati.

David G. Stephan
Director
Industrial Environmental Research Laboratory
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ABSTRACT

This report describes a study to evaluate current baseline performance of hazardous waste incinerators. Tests were conducted at eight full scale facilities to characterize all feed and effluent streams. Pollutants measured included EPA Appendix VIII hazardous compounds, particulates, hydrogen chloride, carbon monoxide, and total hydrocarbons. The data were analyzed to address questions on Destruction and Removal Efficiency (DRE), products of incomplete combustion (PIC), pollutant emission levels, performance of air pollution control systems, and relationships of process parameters to destruction efficiency and emission levels. A large base of data on performance of hazardous waste incinerators was accumulated, and many possible relationtionships between parameters were explored. Conclusions included: DREs were generally above 99.99%; measured DREs tended to be higher when concentration of the hazardous compound in the waste was higher; the most frequently observed PICs were benzene, toluene, chloroform, tetrachloroethylene, and naphthalene; the particulate EPA regulation of 180 mg/Nm^3 was not routinely met; and the hydrogen chloride EPA regulation almost always met.

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The cooperation of all test sites and the efforts of many individuals in Midwest Research Institute's Environmental Systems and Analytical Chemistry Departments are also acknowledged.

APPENDIX A

EVALUATION OF A VOLATILE ORGANIC SAMPLING TRAIN (VOST)

SUMMARY

The results of previous hazardous waste incineration trial burns have suggested that volatile principal organic hazardus constituents (POHCs) are important components in the incineration effluents. The sampling technique initially proposed for the volatile components was the use of an integrated gas bag. This technique, however, suffers from low sensitivity, leakage problems, adsorption losses, and contamination problems.

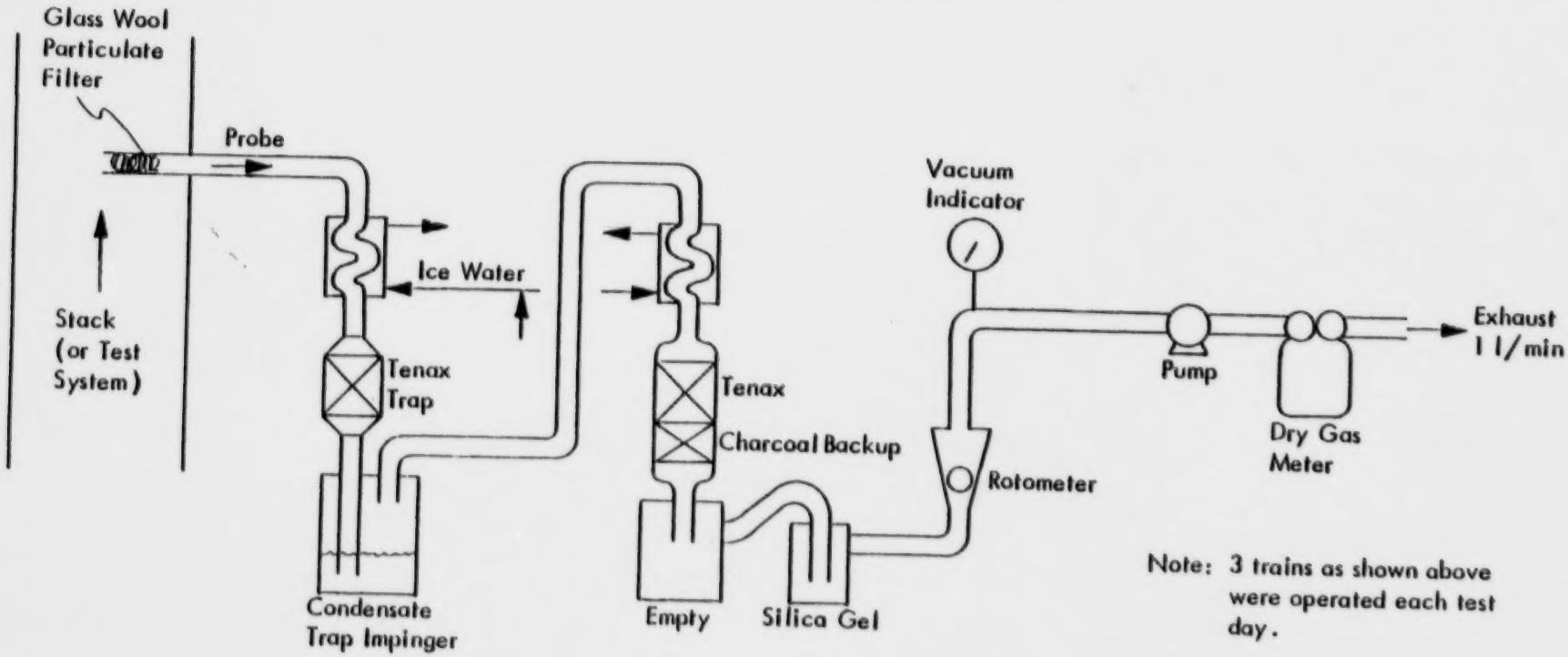
To address the need for a better sampling and analysis technique for volatile POHCs, a meeting was held on April 13, 1982, at which personnel from the Environmental Protection Agency (EPA) and several contracting laboratories discussed concepts for a volatile organic sampling train (VOST). One of the concepts was adopted for development in the laboratory. The purpose of the VOST development effort was to provide a method to collect a sufficient quantity of POHCs to enable calculation of destruction/removal efficiencies (DREs) as high as 99.999% for incinerators whose waste feed contains as little as 100 ppm of a subject POHC. Briefly, the concept adopted involved the following:

1. Sample gas at a flow rate of 1 L/min through a sample collection train having the following basic components as shown in Figure A-1.

- Condenser.
- Front Tenax trap (1.6 cm diameter and 10 cm long, containing 1.6 g of Tenax sp).
- Impinger (for condensate removal).
- Back Tenax/charcoal trap (1.6 cm diameter and 10 cm long, containing 1 g of Tenax and 1 g of charcoal).
- Flowmeter, pump, dry gas meter, etc.

2. Change front and back traps every 20 min (i.e., 20 L of sample) over a 2-hr period, yielding 6 pairs of traps.

3. Analyze one pair (front and back trap individually) by GC/MS. If the POHCs are not present at levels high enough to quantify on the individual traps, combine the contents of the other 5 pairs of traps onto 1 pair by thermal desorption/adsorption, followed by analysis of the resulting single pair by GC/MS.



Note: Tenax & tenax/charcoal traps were 1.6 cm in diameter & 10 cm long

Note: 3 trains as shown above were operated each test day.

Both traps were changed out every 20 minutes over 2 hour period.

Figure A-1. Volatile organic sampling train (VOST).

An evaluation of the above concept was carried out that required the following:

- Set up a system to generate a hot wet gas containing four volatile POHCs (vinyl chloride, carbon tetrachloride, trichloroethylene, and chlorobenzene) at the four different concentrations levels of 0.1, 1.0, 10.0, and 100 ng/L of gas.
- Construct three identical sampling trains to operate simultaneously and draw gas from the above gas generation system.
- Carry out 10 tests using the above three trains and gas generation system.
- Analyze the adsorbent traps after each test, combining several pairs onto 1 pair for the tests at the lower concentration levels.
- Evaluate results, comparing the analysis results with expected values computed for the gas generation system from which the samples were taken.
- Report all results to the EPA project officers by phone within 30 days.

All of the above work was carried out within the specified time. The results showed that the VOST and associated analytical method can detect volatile POHCs at concentrations as low as 0.1 ng/L, but with some variability in results. The variability was greatest for vinyl chloride and carbon tetrachloride at the lowest concentration level, and it was found that blank values for carbon tetrachloride were high relative to the lowest concentration level.

The results revealed that the quantity of a POHC determined for the combined traps from any one train might range from 38 to 173% of the expected value, but that the average of 3 sets of traps from three trains ranged from 48 to 146% of the expected value. In effect, the method easily permitted differentiating between a DRE of 99.99% and 99.999% (with the possible exception of carbon tetrachloride) since these represent an order of magnitude difference which is much greater than the variability noted above. However, the variability in the computed DRE, based on the variability in the averages from the three trains used at all the different concentration levels, was as follows:

DRE (%)	Example variability in reported DRE (%) using VOST
99.9	99.85 - 99.95
99.99	99.985 - 99.995
99.999	99.9985 - 99.9995

HCl was added to the wet gas stream during one run to simulate the composition of some incinerator effluents. The results from this run showed that HCl had no discernible effect on the operation of the train or the POHC levels.

The project also included some investigation relative to the stability of the traps after they had been used for sample collection and the period intervening before analysis. As a result, it was concluded that traps should be analyzed within 2 weeks after samples are collected.

One of the major problems first encountered during this project was determining the best method to analyze wet traps. The method selected which gave reasonably good results, involved thermally desorbing the contents of the adsorbent traps into a purge and trap apparatus (i.e., the apparatus used for EPA Method 624). However, there was not sufficient time to evaluate other techniques that could be used.

A number of mechanical problems were identified during this evaluation, including leak-checking of traps and attendant breakage of the glass traps. This problem and others, such as contamination of the outer surface of the traps in the field, will require an improved trap assembly and connector for use of the VOST in the field.

After all the results from this evaluation had been compiled they were discussed in detail with the EPA project officers. Their concensus was that the method should be subjected to a field test, although there were some details that needed to be clarified. The VOST was used as part of a field test which was conducted in early June.

SECTION 1.0

INTRODUCTION

Members of EPA and personnel from several contract organizations met on April 13, 1982, to develop a concept for a volatile organic sampling train (VOST). The objective of this sampling train and the subsequent GC/MS analysis was to enable determination of DRE at the 99.999% level for volatile POHCs when firing waste containing as little as 100 ppm of those POHCs in hazardous waste incineration facilities.

A laboratory study was carried out to evaluate the sampling train concept developed during the meeting. This appendix describes how the laboratory evaluation was performed and presents the results of the evaluation and conclusions and recommendations based on the results.

SECTION 2.0

CONCEPT

The VOST concept to be evaluated consisted of a system designed to draw effluent gas at a flow rate of 1 L/min through two traps* in series (see Figure A-1). The first trap contained Tenax and was preceded by a gas cooler/condenser and followed by an impinger for condensate collection. A second trap containing a section of Tenax and a section of charcoal was located after the impinger. The purpose of the second trap was to collect highly volatile POHCs (e.g., vinyl chloride), which readily break through a Tenax trap. In addition, the concept involved replacing both pairs of traps with fresh traps every 20 min (i.e., 20 L of sample) over a 2-hr sampling period. There were two basic reasons for changing the traps every 20 min:

- At sample volumes of greater than 20 L, some of the very volatile POHCs will break through both the front and backup adsorbent traps.

- The changing of the traps allows an initial analysis of one pair of traps. Analysis of a single pair of traps lowers the possiblity of collecting too much sample and overloading the GC/MS system. However, if the POHCs are not detected or are present at low levels in the single pair, the option exists of combining the contents of the remaining pairs of traps onto one pair of traps with a concomitant increase in sensitivity. The advantage of the second option for samples with low POHC concentrations is given below.

If a hazardous waste incineration facility is achieving a DRE of 99.999% for a POHC that is present in the waste at a concentration as low as 100 ppm, the resulting concentration of that POHC in the flue gas will be approximately 0.1 $\mu g/m^3$ or 0.1 ng/L. Sampling 20 L of that gas will collect only 2 ng of the POHC on a single pair of traps. Since 2 ng may not be detectable by GC/MS analysis, the concept required collection of several (e.g., five) additional pairs of traps and the desorption of their contents onto another pair of traps, thereby providing a total of 10 ng for GC/MS analysis.

It is anticipated that when the VOST system is used in the field, one will not know if pairs of traps should be analyzed individually or if several pairs should be desorbed onto one pair. That is, if the concentration

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* Traps were 1.6 cm in diameter x 10 cm long.

of the volatile organic in the effluent is low (e.g., 0.1 to 1.0 ng/L), several pairs should be desorbed onto one pair for analysis. However, if the concentration is high, the pairs should be analyzed individually, since desorption of the contents of several pair onto one pair would make the quantity even larger and saturate the GC/MS detector. Therefore, the intent is to use the VOST to collect 6 pairs of sample traps, but with one pair being analyzed first, individually, to determine the amount present. Then, if warranted, the contents of some or all of the remaining pairs can be desorbed onto one pair for analysis.

One question that may arise in the mind of the reader is: "Why is it necessary to use a pair of traps, one being Tenax and one Tenax/charcoal?" To answer this, it must be noted that charcoal is a good adsorber for highly volatile organics, but compounds that are less volatile are not easily desorbed from charcoal. On the other hand, the adsorptivity of charcoal decreases when it is wet. Thus, the dual trap configuration was considered best to cover all possibilities. But, it is possible that further work might show that a single Tenax/charcoal trap, after a condensate separation impinger, might be just as effective. (Results of this evaluation, using the dual traps, did show that most of the vinyl chloride was present on the Tenax/charcoal trap, whereas most of the other three compounds was present on the first Tenax trap.)

In concert with the EPA project officers, a plan was developed to evaluate the VOST concept that consisted of the following:

- Set up an experimental system to generate a wet gas stream spiked with four volatile POHCs at each of four different concentration levels.
- Construct three identical VOSTs that would simultaneously draw gas from the spiked gas stream.
- Set up equipment for conditioning traps and for thermally desorbing several pair onto one pair.
- Set up equipment for analyzing traps by GC/MS.

After the above equipment had been set up and made operational, the plan consisted of carrying out a series of 10 tests. The test runs included: tests at each of the four concentration levels, replicate tests at one level, blanks, and a test (also at the replicate level) where the gas contained HCl. The purpose of this last test was to determine if HCl, which is present in many incinerator effluents, had any effect on the analysis results. The sequence of the tests in this plan was as follows:

Test	Level (concentration of POHCs in gas)	Comment
1	III (10 ng/L)	Exploratory run to check system
2	0 -	Blank run
3	III (10 ng/L)	
4	I (0.1 ng/L)	
5	II (1.0 ng/L)	
6	IV (100 ng/L)	
7	0 -	Blank run
8	II (1.0 ng/L)	Duplicate of Run 5
9	II-HCl (1.0 ng/L)	Duplicate of Run 5 with HCl in gas
10	0 -	Blank run

The equipment used in carrying out the tests is described in the next section.

SECTION 3.0

DESCRIPTION OF EQUIPMENT AND PROCEDURES

This section contains descriptions of the equipment and procedures in the following order:

3.1 Gas Generator System

3.2 Sampling Trains (VOST)

3.3 Trap Conditioning/Desorption Apparatus

3.4 Trap Desorption/Analysis Equipment

3.5 Analytical Procedures

3.1 GAS GENERATION SYSTEM

As shown in Figure A-2, the gas generation system consisted of 1/2-in. stainless steel tubing to carry vaporous N_2 from a liquid N_2 tank through a heater, where the N_2 was heated to about 300°F. At that point, the N_2 was made "wet" by vaporizing deionized/charcoal filtered water fed through a quartz tube heater. Also near that point, the liquid containing the four POHCs was pumped by a syringe pump (5 mL/hr) into the hot N_2 stream where it immediately flashed to a gas.

The liquid injected by the syringe pump was a solution of the four POHCs in methanol.

The four POHCs selected were:

- Vinyl chloride;
- Carbon tetrachloride;
- Trichloroethylene; and
- Chlorobenzene.

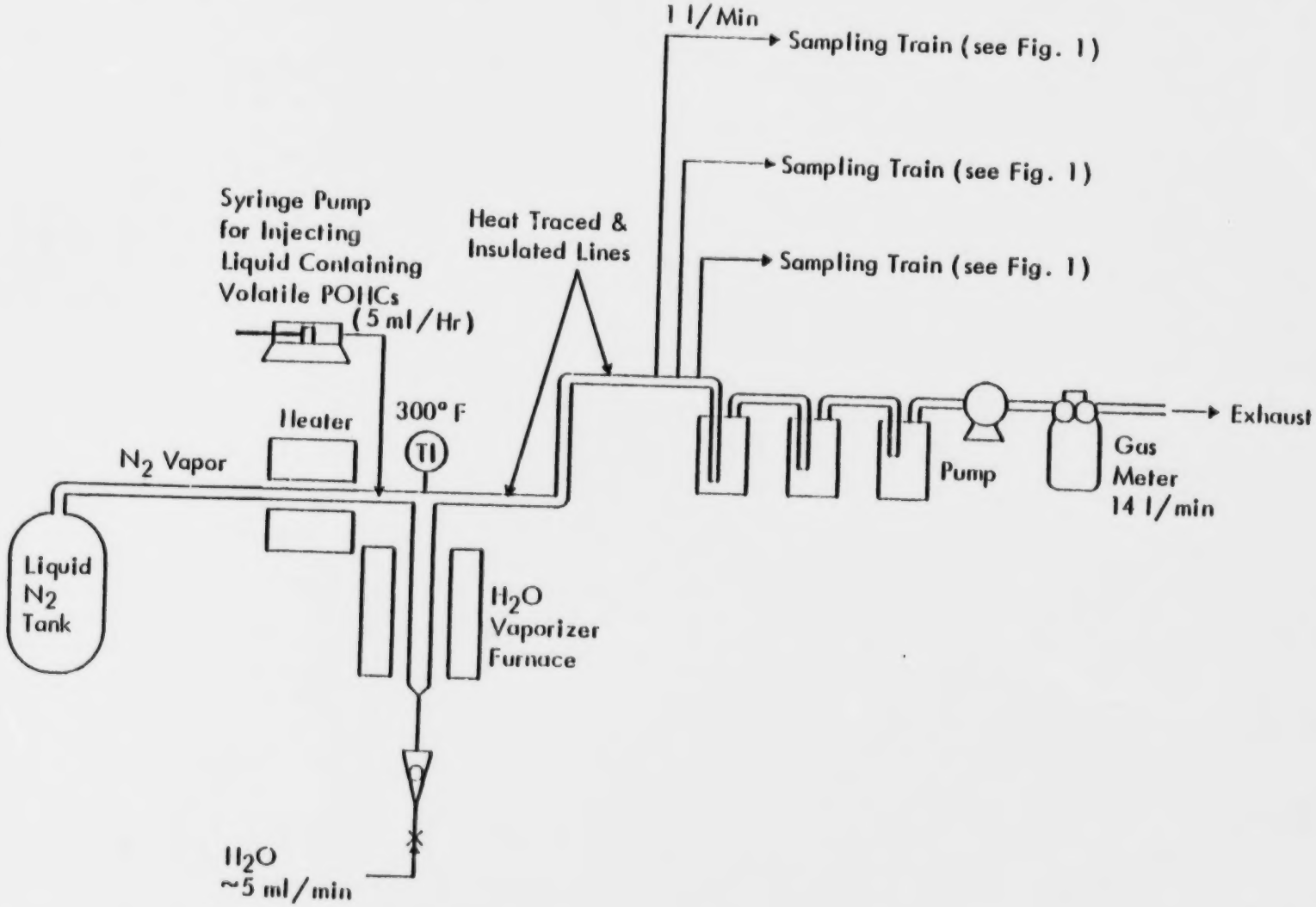

Figure A-2. Schematic diagram of apparatus used to generate and sample a hot wet gas stream containing volatile POHCs.

Concentrations of each of the four POHCs were:

Level	Concentration in methanol solution (ng/mL)	Expected conc. in gas stream (ng/L)	Expected amount in each pair of traps (ng)
I	84	0.1	2
II	840	1.0	20
III	8,400	10.0	200
IV	84,000	100.0	2,000

The solution with the highest concentration (Level IV) was prepared first, then aliquots were serially diluted with methanol to prepare the three lower concentration solutions. These same solutions were used as calibration standards for the subsequent analyses.

Following the steam and POHC solution injection point, the gas stream entered a sampling manifold, with a perforated dispersing plate at the inlet. Gases were drawn from this manifold into the three sampling trains. After the manifold, the hot gas (11 to 12 L/min) passed through a series of impingers (for water removal) and on through a pump and dry gas meter.

During each of the tests, the gas generation system operated quite well, and all readings were consistent from run to run. The water content of the gas stream ranged from 35 to 37 volume percent, as measured by the impingers and gas meter.

During Run 9, HCl was added to the water at a level of 1.3 g of HCl per liter of water to provide an HCl concentration in the gas of about 0.5 g/Nm^3. This is the HCl concentration estimated to occur in the effluent from an incinerator burning a waste containing 15% Cl and equipped with a wet scrubber operating at the relatively low HCl removal efficiency of 95%.

The gas flow rate in the gas generator system and the POHC syringe pump injector rate were used to compute an "expected value" for the quantity of each POHC in the Tenax traps. It was not feasible within the scope and time frame of this project to quantify the actual concentration of the POHCs in the gas produced by the gas generator system. An independent analysis of the spiked gas stream would have been desirable; however, the subsequent VOST data gave little or no reason to believe that the actual gas stream concentrations were significantly different than the computed "expected values."

3.2 SAMPLING TRAINS (VOST)

Figure A-1 showed the VOST configuration that was evaluated. The train consisted of:

- A sampling line (1/4-in. Teflon tubing in the test system);
- First condenser;
- Tenax trap;
- Impinger (for condensate removal);
- Second condenser;
- Tenax/charcoal trap; and
- Other sampling components (rotameter, pump, dry gas meter).

Except for the Teflon sampling line, most of the components were made of glass, including the traps. However, the fittings at the inlet and outlet of each trap were stainless steel.

When the trains were initially assembled, two problems developed. First, the 1-in. stainless steel Swagelok fittings for the inlet of the traps were designed to slip over the glass trap, but some of the traps had an outside diameter slightly larger than the inside diameter of the Swagelok nut. Thus, all the nuts had to be drilled out. Secondly, some of the glass traps were out-of-round. This meant that some traps, when inserted into the sampling train, would not leak-check unless the fittings were tightened with wrenches. Several tubes broke before they could be tightened enough to pass a leak-check. Since checking for leaks and correcting of leaks can take considerable time, this could potentially be a more serious problem in the field unless the trap connections are redesigned.

Before each run, the gas generation system was started up and allowed to operate for about 1 hr. During that time, traps were connected in the three trains and leak checked. All three trains were then started and operated for 20 min at about the same rate (1 L/min).* All three sampling trains were then shut off and the traps removed and placed in premarked container tubes. Another pair of traps were then inserted in each train and leak-checked before starting the next 20-min sampling period. A run was considered complete after 6 pairs of traps had been used in each train. During each run, ice water was circulated through the condensers. Thermocouples, located against the surface of the condenser outlet tubes, indicated that the gas temperature entering the first trap was in the range of 60° to 80°F. (The train with the longest Teflon sampling tube giving the lowest temperature.)

Overall, the train configuration caused no particular difficulty, except for the leak-check problem described above. However, using this train configuration to sample a "wet" gas stream saturates the first trap with condensate. This caused no problems in the sampling but did require development of procedures for analyzing the wet traps, as discussed in the next section.

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* Gas flow rates in liters per minute refers to normal conditions of 20°C, 1 atm (dry basis).

3.3 TRAP CONDITIONER/DESORPTION EQUIPMENT

The trap conditioning/desorption apparatus, purchased from Nutech (Model No. 322, Nutech Corporation, 2806 Cheek Road, Durham, NC 27704), served two purposes for the VOST evaluation. First, it was used to condition traps prior to their use, by heating at 240°C for 30 min with a flow of 30 mL/min of purified nitrogen gas. Second, it was used to thermally desorb the sample contents from each of several pairs of traps onto one pair for GC/MS analysis. The purpose of this desorption/adsorption was, in effect, to concentrate the samples from the sampling train.

A schematic diagram of the conditioning/desorption apparatus is shown in Figure A-3, along with the trapping system that was added at the outlet to re-adsorb the contents from the traps being desorbed.

When four traps were being desorbed (which is the capacity of the equipment), the carrier gas (N_2) exited the desorption chamber hot, but cooled rapidly. However, when the traps being desorbed were wet, the cooling was not nearly so rapid because of the steam that must be condensed. Thus, it was necessary to use a condenser at the outlet of the conditioning equipment, in front of the first trap (Tenax). An impinger was also required to remove the condensate before the desorbed gas passed into the second trap. As a result, the re-adsorption system of traps at the outlet of the desorption equipment is equivalent to the sampling train itself. Also, the condensing steam again wets the first trap, so the need to analyze a wet trap still remains.

When using the Nutech conditioning apparatus to desorb several pairs of traps (e.g., 5 pairs), the conditioner was first heated to its normal operating temperature of 240°C. Four traps were then dropped into the chambers and allowed to remain there for 10 min (with the total N_2 carrier flow of 100 mL/min passing through the four traps). These four traps were then removed and four more traps inserted, repeating the procedure until all 5 pairs had been desorbed onto the one pair at the outlet. This pair, or any pair analyzed individually without first being desorbed, was then spiked with an internal standard and analyzed using the equipment described in the next section.

3.4 TRAP DESORPTION/ANALYSIS EQUIPMENT

Although the results presented later in this report are given for each pair of traps, each trap was actually analyzed individually since the analytical desorption system has only one chamber. The analytical system (shown in Figure A-4) was basically the same as that used for EPA Method 624,except with the major addition of the Nutech Thermal Desorption System (Model 320).

The procedure was to drop the sample trap into the desorption chamber, and quickly close the chamber cap. The tube remained in the chamber for 10 min at a temperature of 180°C. During this period, carrier gas (N_2) flowed through the chamber, up through the purge column containing 1 to 5 mL of water, and into the analytical adsorbent trap. The analytical adsorbent

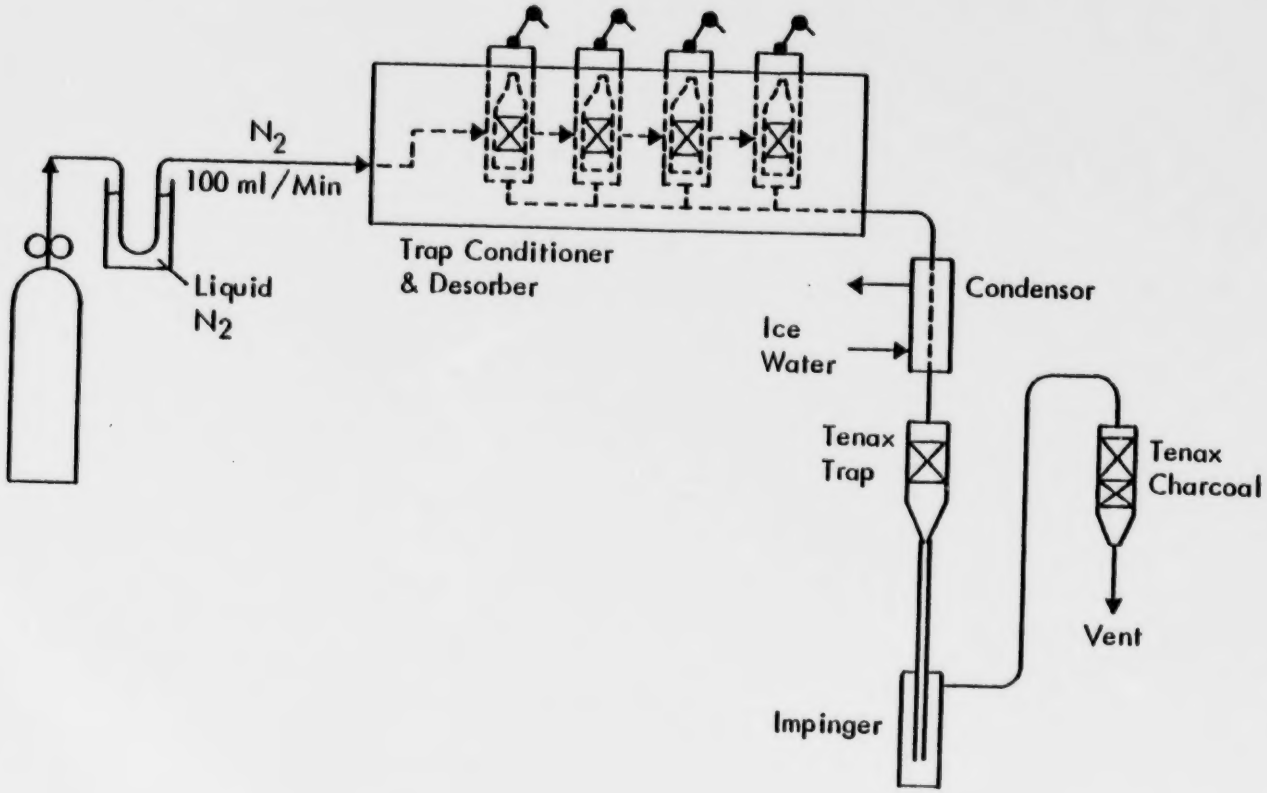


Figure A-3. Schematic diagram of trap conditioner/desorption apparatus.

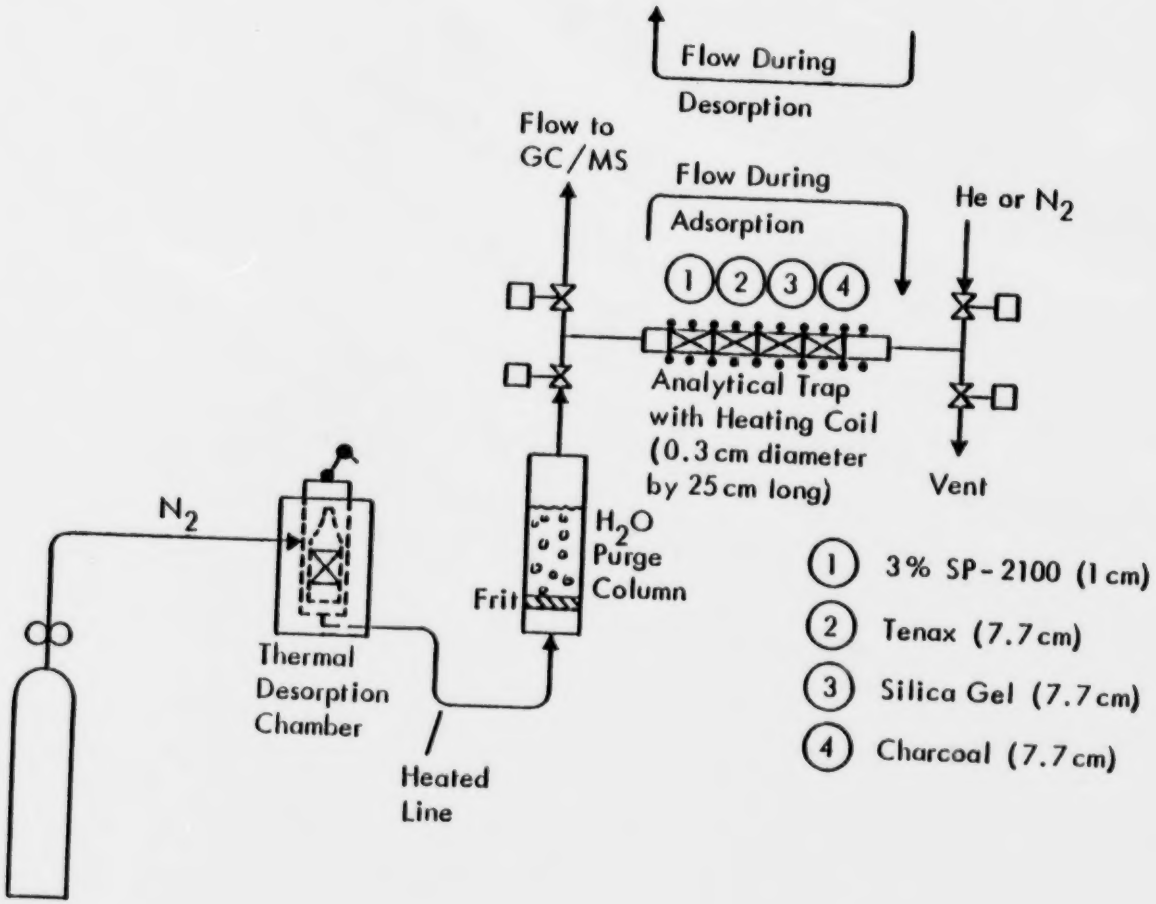


Figure A-4. Schematic diagram of trap desorption/analysis system.

trap consisted of a 25- x 0.3-cm diameter stainless steel tube packed with 1 cm of 3% SP-2100, 7.7 cm Tenax, 7.7 cm silica gel, and 7.7 cm of charcoal. Following the 10-min desorption period, the analytical adsorbent trap was rapidly heated to 180°C with the flow through the analytical trap reversed, so that the outlet flow from the analytical trap was directed into the GC/MS.

3.5 ANALYTICAL PROCEDURES

The analytical procedures described below include cleanup of the Tenax and charcoal prior to packing into traps, preparation of the traps, conditioning of the traps prior to sampling, spiking of the traps with an internal standard following sampling, GC/MS analysis of the traps, and data reduction.

3.5.1 Tenax and Charcoal Cleanup

The Tenax (35/60 mesh) and SKC petroleum-based charcoal (Lot No. 104) were initially prepared by Soxhlet extraction for 24 hr with methanol and then with pentane. The sorbents were then dried in a vacuum oven at 110°C for 6 hr. (Some residual pentane remained in the Tenax for several analyses, and therefore it is not recommended for cleanup of the Tenax or charcoal in any subsequent work of this type.)

3.5.2 Preparation of Traps

The 10- x 1.6-cm glass traps with one nippled end (to facilitate removal of the traps from the desorption apparatus with tweezers) available from the Nutech Corporation were used for the VOST evaluation. A minimum amount of pre-extracted and oven-dried glass wool was used in each of the glass tubes to hold the sorbents in the glass traps. The all-Tenax traps contained about 1.6 g of Tenax, and the Tenax/charcoal traps contained about 1 g of Tenax and 1 g of charcoal (two-thirds Tenax by volume).

3.5.3 Trap Conditioning

The traps were thermally conditioned prior to use, using the Nutech Model 322 thermal conditioning unit. The conditioning gas (nitrogen or helium) was purified by passing through a U-trap containing a 5-Angstrom molecular sieve with the U-trap immersed in liquid nitrogen. The temperature of the conditioning unit was adjusted to 240 to 250°C, and the flow rate of gas through each trap was estimated to be about 30 mL/min. Only the sum of the flow through four of the traps, which was set at 120 mL/min, could actually be measured with the Nutech conditioning unit. The traps were conditioned for at least 6 hr prior to their first use in the VOST evaluation and for at least two additional hours prior to use in sampling.

Following conditioning, each trap, which was engraved with a unique number, was transferred to a clean 25- x 150-mm screw-cap test tube engraved with the same unique number. The traps were then ready for sample collection or spiking experiments.

3.5.4 Spiking of Traps with Internal and Calibration Standards

Prior to GC/MS analysis, all Tenax and Tenax/charcoal adsorbent trap samples and standards were spiked with 25 ng of perfluorobenzene internal standard using the flash vaporization technique in which the spiking solution was vaporized and carried onto the trap with a carrier gas. The glass traps were attached to the injection port (160°C) of a GC with a 1-in. stainless steel Swagelok nut containing Teflon ferrules. The Swagelok fitting was connected to the GC column connection via a reducing fitting. The helium flow through the traps was set to about 50 mL/min. The gas flow through the trap was turned on and off using the shut-off valve on the side of the Varian 1400 GC.

The spiking solution was loaded and expelled from the syringe using the solvent flush technique. To use this technique, the needle of a 5.0-μL syringe was filled with clean methanol. Then air was drawn into the syringe to the 1.0-μL mark followed by a 25-ng/μL methanolic solution of the PFB to the 2.0 μL mark. The gas flow was turned on through the trap and the syringe needle injected through the GC septum port. The contents of the syringe were then slowly expelled over about a 15-sec period. At the end of about 25 sec, the gas flow through the trap was shut off and the syringe removed. All POHC calibration standards were spiked using exactly the same procedure. The total flow of gas through the traps during spiking was thus only about 25 mL.

3.5.5 GC/MS Analysis of the Traps

The trap samples were analyzed by GC/MS using the following procedures:

1. Prepare the purge-trap-desorb (P-T-D) and GC/MS system for analy- of a trap:

   - Turn 6-port valve on purge and trap system to "purge" mode.
   - Cool analytical trap containing Tenax, silica gel, and charcoal to ambient temperature.
   - Ensure flow rate of helium through Nutech desorption unit and purge column is 40 mL/min.

2. Insert adsorbent trap (large end down) into the Nutech desorption unit. Immediately close Nutech lid and start stopwatch.

3. Enter the data acquisition information in the GC/MS data system.

4. At the end of 10.0 min immediately:

   - Switch purge and trap 6-port valve to the "desorb" mode.
   - Heat the analytical trap to 180°C.
   - Start the GC program (40°C for 3 min, then temperature program to 175°C at 8°C/min (column was 2 m x 2 mm ID glass column packed with 0.2 % Carbowax 1500 and 60/80 mesh Carbopak C).

5. At the end of the GC/MS run:

- Turn off heat to the analytical column. Switch 6-port valve back to the "purge" mode.

The purge and trap GC/MS system was then ready to analyze another adsorbent tube sample.

The normal routine for analyzing a set of traps from each of the laboratory VOST evaluation runs was to analyze a calibration standard on Tenax, a calibration standard on Tenax/charcoal, and then to intersperse calibration standards about every fourth sample. Blank Tenax and blank Tenax/charcoal traps (conditioned traps spiked with internal standard) were also analyzed when the samples from the blank VOST train were analyzed. The same POHC solution used to spike the wet gas in the VOST runs was used to prepare the calibration standards for quantification of the POHCs on the traps.

Although the Nutech system is not normally used in the purge-trap-desorb configuration used on this project, it provided a means of overcoming the problem of analyzing wet traps by a method that offered minimal risk of losing or affecting the very small amounts of each compound to be quantified (i.e., 2 to 10 ng of POHC). Since this purge and trap technique initially appeared to work and was basically consistent with an accepted EPA method, it was used in this evaluation. The Nutech was initially used in the cryogenic trapping configuration, but the desorbed water froze and clogged the analytical system. Other techniques were considered but not investigated because of lack of time and possible associated problems. Further work may show that other techniques can be used to advantage.

3.5.6 Data Reduction

The POHCs in the samples were quantified using the internal standard technique. The area of the masses of m/z 62 for vinyl chloride, m/z 117 for carbon tetrachloride, m/z 130 for trichloroethylene, m/z 112 for chlorobenzene, and m/z 186 for the perfluorobenzene were used to calculate response factors from analysis of the 8.4- and 84-ng calibration standards according to the equation:

$$\text{Response Factor (RF)} = \frac{(A_S)\ (C_{IS})}{(A_{IS})\ (C_S)}$$

where:
A_S = The area of the ion for the POHC.
A_{IS} = The area of the ion for the internal standard (m/z 186).
C_{IS} = The amount of internal standard (25 ng).
C_S = The amount of POHC in the calibration standard (generally 8.4 or 84 ng).

The amounts of the POHCs in the samples were then calculated according to:

$$\text{Amount of POHC} = \frac{(A_S)\ (C_{IS})}{(A_{IS})\ (RF)}$$

The reproducibility of the internal standard area counts (m/z 186) was very good with an average variation of about 10% for a daily batch of samples at a given multiplier setting. There does not appear to have been any particular difference in perfluorobenzene area counts with the type of trap, e.g., wet traps or Tenax/charcoal traps did not give lower area counts than dry traps and Tenax-only traps. This was in contrast to the POHC vinyl chloride which gave higher response on Tenax than on Tenax/charcoal traps during analysis of calibration standards. With only 25 mL of gas passed through the trap during spiking, no reason for the vinyl chloride passing through the Tenax to the charcoal was determined.

SECTION 4.0

PRESENTATION AND DISCUSSION OF RESULTS

It was noted in Section 2.0 that a total of 10 runs was made during this evaluation, involving four different concentration levels of the POHCs and three blank runs. After each run, the traps from each of the three trains were analyzed and results reported for the traps as pairs (i.e., Tenax trap plus Tenax/charcoal trap). Not all pairs were analyzed, especially at the higher concentration levels, where it was not necessary to desorb several pairs onto one pair. In most cases, at the lower concentration levels, a pair of traps from each train were analyzed individually, and all remaining pairs from each train were desorbed onto a single pair for analysis. This is important to remember in evaluating the results, and it should be noted that several calibration standards were analyzed along with the traps from each run.

Results were initially calculated after each run based on calibration standards analyzed with the samples from each run. After all runs and analyses had been completed, results were recalculated based on the average response factor using the internal standard technique described earlier in Section 3.5.6. These reponse factor data are shown in Table A-1. Data in Table A-1 also show transfer efficiencies determined for desorbing several pairs of traps with re-adsorption onto a single pair. Since the transfer efficiency for vinyl chloride was relatively low (49%), measured values for vinyl chloride were corrected for this. Also, almost all the data for all four POHCs were blank corrected, as discussed below.

Three blank runs were carried out using the gas generation system and three trains, but without any injection of solution containing the POHCs into the system. Results for these blank runs are shown in Table A-2 and include analysis of single pairs, and several pairs combined onto one pair. As can be seen in Table A-2, most of the blank values are relatively low, but are still significant relative to a run at the lowest concentration level where the expected amount of any POHC on each pair is only about 2 ng. In this regard, the blank values for carbon tetrachloride in Runs 7 and 10 are greater than the expected value. Thus, it was not possible to blank correct the carbon tetrachloride results obtained in the lowest level run (Run 4), which makes it difficult to make any definitive conclusions about using the VOST train for detecting such low levels of carbon tetrachloride.

The problem with the high carbon tetrachloride blanks was evident after Run 7, and therefore another blank run was made (Run 10), preceded by purging of the gas generation system and the trains with vapor from the liquid

TABLE A-1. GC/MS RESPONSE FACTOR AND THERMAL DESORPTION COLLECTION EFFICIENCY FOR FOUR VOLATILE POHCs

Compound	Ave RF[a]	σ	% RSD[b]	n[c]	Type of trap	RF[f] following desorption	n	Desorption transfer efficiency
Vinyl chloride	0.140	± 0.042	30	15	T/C[d]	0.069	2	49
Carbon tetrachloride	0.197	± 0.069	35	13	T[e]	0.143	2	73
Trichloroethylene	0.490	± 0.068	14	14	T	0.435	2	89
Chlorobenzene	0.338	± 0.065	19	14	T	0.331	2	98

[a] Mass spectrometric response factor relative to perfluorobenzene.

[b] RSD = Percent relative standard deviation, which equals σ ÷ Mean x 100.

[c] n = Number of determinations (includes 8.4 and 84 ng calibration standards).

[d] T/C = Tenax/charcoal (~ 70:30 v/v).

[e] T = All tenax trap (1.6 g).

[f] Contents of calibration standard thermally desorbed onto type of adsorbent trap in previous column.

TABLE A-2. TABULATION OF DATA FROM BLANK RUNS

Blank run No.	No. of combined pairs	Amount detected (ng)[a] Vinyl chloride	Carbon tetrachloride	Trichloro-ethylene	Chloro-benzene
		Single pairs data			
2		----------	No single pairs analyzed		----------
7		< 0.5	12.5	0.7	0.8
7		< 0.5	3.6	0.2	0.6
7		< 0.5	3.5	< 0.5	< 0.5
10		< 0.5	1.2	3.4	< 0.5
10		< 0.5	3.7	< 0.5	< 0.5
10		< 0.5	< 0.5	2.0	< 0.5
Avg. for single pairs[b]		0	4.1	1.1	0.2
		Combined pairs data			
2	4	5.4	< 0.5	2.3	8.0
2	4	4.8	< 0.5	2.5	6.4
7	5	4.7	35	5.0	8.1
7	5	1.1	49	6.6	10.0
7	5	Lost	17	6.3	4.0
10	5	< 0.5	53	4.8	1.8
10	5	< 0.5	50	2.2	3.6
10	5	< 0.5	54	3.0	6.2
Average per pair for combined pairs		0.5	6.8	0.9	1.3

a Amounts calculated based on average response factor determined from all standards (response factor for VC was based on analyzing standards on Tenax/charcoal traps; the other compounds were based on analyzing standards on Tenax traps).

b Less than values were assumed to be zero in order to compute an average.

N_2 tank at room temperature for 24 hr. However, the blank carbon tetrachloride values were again found to be high in Run 10. Other blank traps were analyzed which had not been exposed to the gas generation system, but had been exposed to room (laboratory) air, and no POHCs were detected in these blanks (i.e., < 0.5 ng). From this and other blank runs during the project, it appears that the high blank values for carbon tetrachloride resulted from the gas generation system or the sampling trains, but was not a result of any subsequent analytical procedures.

Except for the carbon tetrachloride data from the lowest level run, all uncorrected and blank corrected results were tabulated, with the corrected values being used to compute the results as a percentage of the expected value. These tabulated data are shown in Section 6 and have been summarized in Table A-3.

Data in Table A-3 provide information on results computed as averages but do not show the range in results. Tables in Section 6 contain all results but are difficult to intercompare. Therefore, the data in Section 6 were used to prepare Figures A-5 through A-8 showing the results for each POHC in all runs, as discussed below.

4.1 VINYL CHLORIDE

Figure A-5 (for vinyl chloride) shows all results, blank corrected and corrected for the 49% transfer efficiency when transferring contents of several pairs of traps onto one pair.

Results for vinyl chloride at the two lowest concentration levels appear to be similar, with single pairs mainly found to be less than the expected value, and combined pairs evenly distributed from 40% of the expected value up to about 160% of the expected value. Conversely, at the next highest level where only single pairs were analyzed, all except one data point are greater than the expected value, ranging from 100 to 180% of the expected value. This is a rather wide range, but vinyl chloride is very volatile, and it is commonly recognized that analyses for this compound are difficult.

At the highest concentration level (Level IV or ~ 2,000 ng/pair), the results were consistently low. Nearly all of the other POHCs were always found on the first Tenax trap of any pair, but most of the vinyl chloride was always found on the second Tenax/charcoal trap. It therefore is concluded that breakthrough of the vinyl chloride occurred at this highest concentration level. Thus in any further testing, one should be aware that this may occur when using the VOST method at high concentrations of vinyl chloride.

4.2 CARBON TETRACHLORIDE

Results for carbon tetrachloride are shown in Figure A-6. These results are all blank corrected data except for the data at the lowest concentration level. As a consequence, the data at Level I exhibits some very high values, which undoubtedly are not representative.

TABLE A-3. VOST DATA SUMMARY

Run No.	Expected gas phase concentration of each compound (ng/liter)[a]	No. of cartridge[b] pairs analyzed (i.e., replicates)	No. of cartridge[b] pairs combined for analysis	Average expected value (ng)	Average amount found, in ng, - blank corrected,[d] and (%[d] of average expected value)							
					Vinyl chloride[c]		Carbon tetrachloride[d]		Trichloroethylene		Chlorobenzene	
					Single pairs	Combined pairs	Single pairs	Combined pairs	Single pairs	Combined pairs	Single pairs	Combined pairs
2	0	2	4	0	-	5.1		< 0.5		2.4		7.2
7	0	3	0	0	< 0.5		6.5		0.3		0.5	
7	0	3	5	0		2.9		34		6.0		7.4
10	0	3	0	0	< 0.5		1.6		1.8		< 0.5	
10	0	3	5	0		< 0.5		52		3.3		3.9
4	0.1	2	0	1.9	1.5(79%)		4.2(221%)[d]		1.5(79%)		1.8(95%)	
4	0.1	3	5 (4 in 1 set)	9.1		10.1(111%)		16(176%)[d]		8.8(97%)		9.5(104%)
5	1.0	3	0	19	12(63%)		9(47%)		22(116%)		29(153%)	
5	1.0	3	4	77		37(48%)		68(88%)		83(108%)		101(131%)
8	1.0	3	0	20	17(85%)		11(55%)		23(115%)		21(105%)	
8	1.0	3	4	79		115(146%)		89(113%)		83(105%)		91(115%)
9	1.0 (with HCl)	3	0	20	19(95%)		8(40%)		19(95%)		18(90%)	
9	1.0 (with HCl)	3	4	77		61(79%)		85(110%)		81(105%)		74 (96%)
3	10.0	7	0	193	274(142%)		136(70%)		210(109%)		204(106%)	
3	10.0	-	0	-		-		-		-		-
6	100.0	6	0	2,020	870(43%)		2,180(108%)		2,660(132%)		2,050(101%)	
6	100.0	-	0	-		-		-		-		-

[a] Gas volume in liters refers to dry standard conditions (20°C, 1 atm).

[b] Cartridge pairs refers to one Tenax cartridge and an associated Tenax + charcoal cartridge.

[c] Data for vinyl chloride includes correction for 49% transfer efficiency when several pairs are desorbed onto one pair (per Table A-1).

[d] All values are blank corrected except for carbon tetrachloride in Run 4, due to large average blank value (per Table A-2).

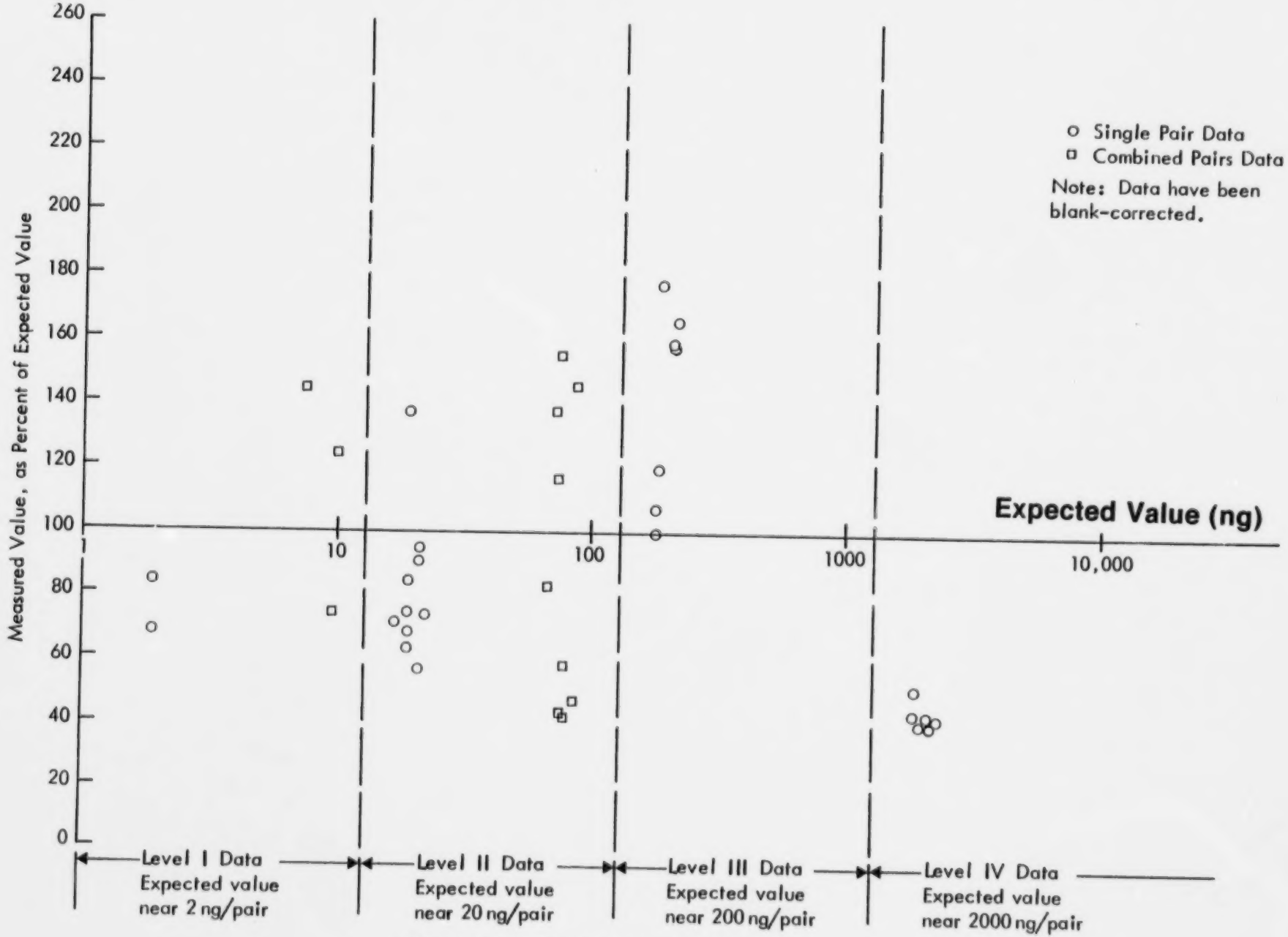


Figure A-5. Vinyl chloride test results.

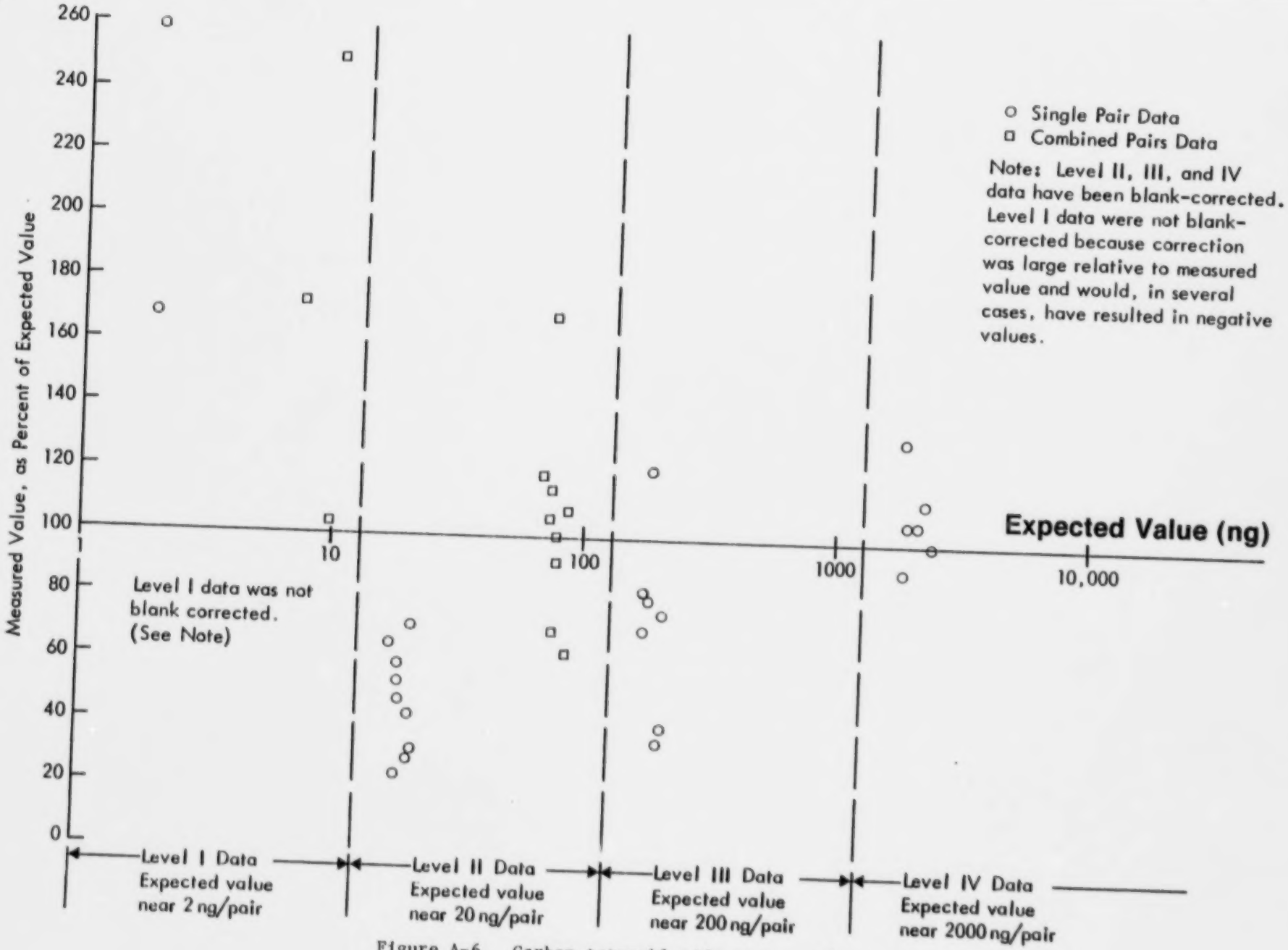


Figure A-6. Carbon tetrachloride test results.

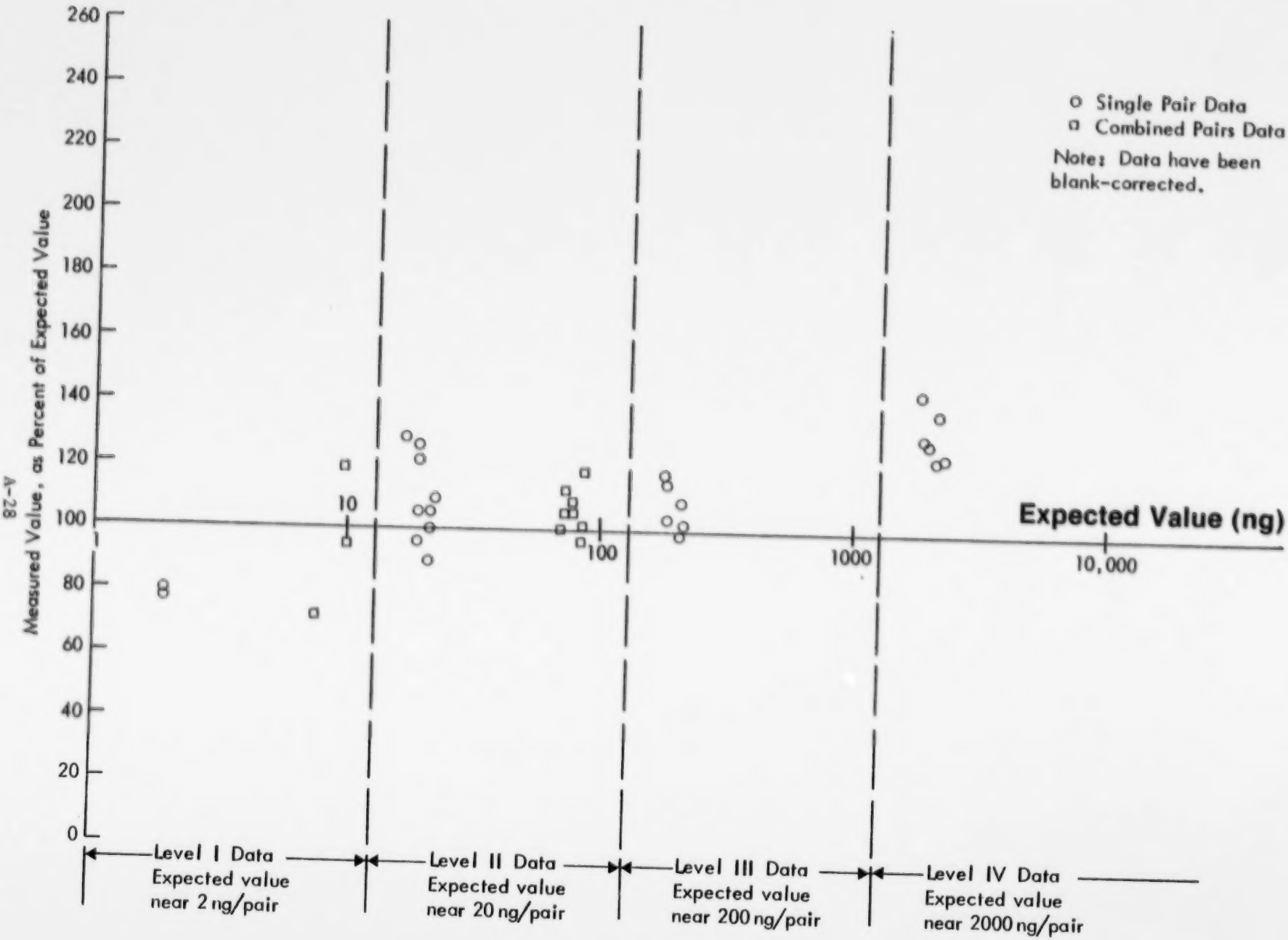


Figure A-7. Trichloroethylene test results.

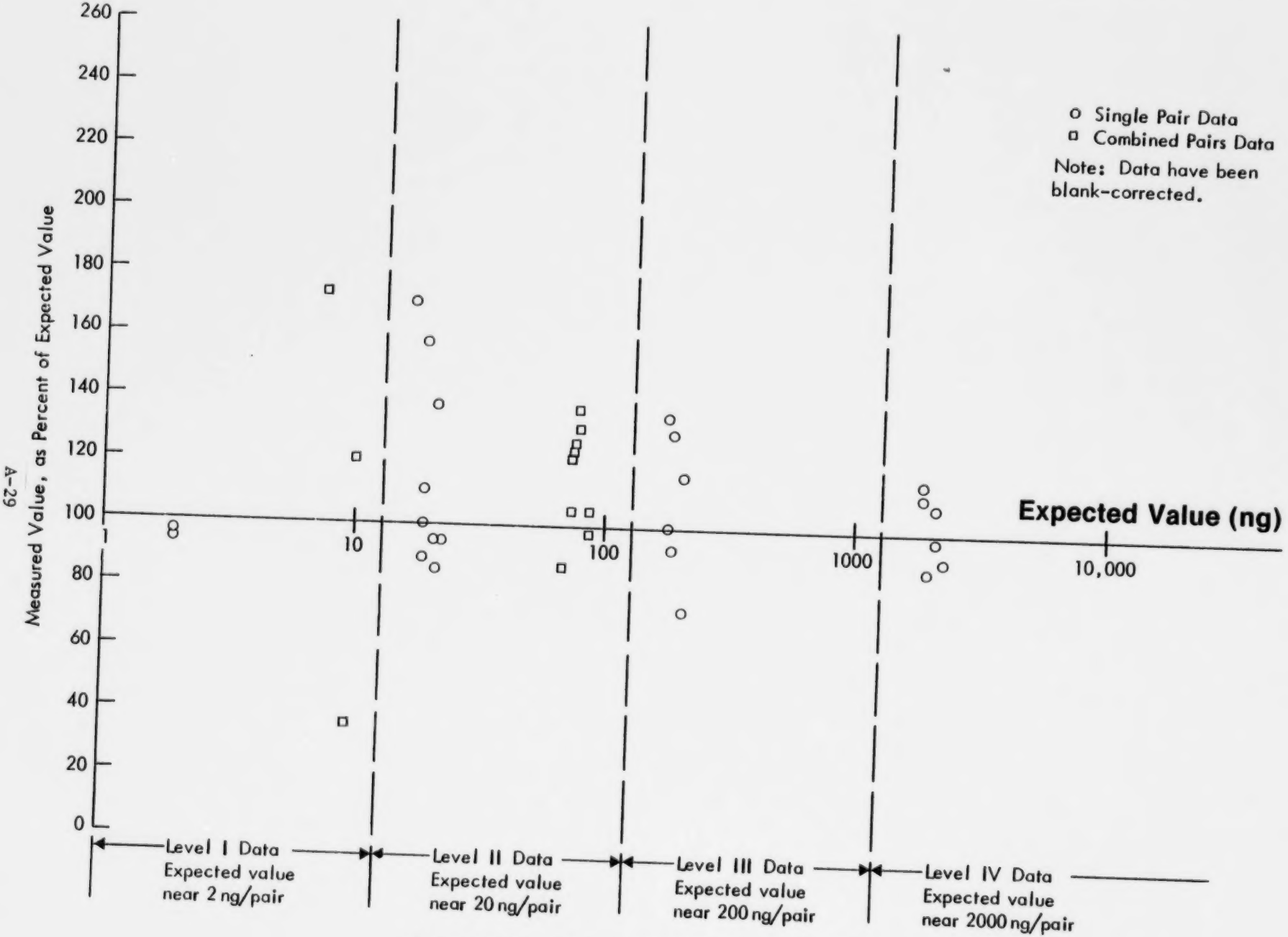


Figure A-8. Chlorobenzene test results.

Data at Level II are similar to vinyl chloride, in that all data for single pairs are less than the expected value, but data for combined pairs range from 60 to 170% of the expected value. This phenomena is not as yet explainable, but most probably relates to the quantity present on any trap being analyzed and the characteristics of the purge-trap-desorb and GC/MS analysis method. As originally conceived, the intent would be to rely on results for combined pairs at low levels, which does seem to be supported by the data.

At Level III, data for all the single pairs, except one, were less than the expected value, ranging from 36 to 120%. Thus, a result for any single pair might be quite low, but it is anticipated that, in any future field testing with the VOST emission, results would be based on analysis of several pairs, which in this case would have yielded an average value of 70% of the expected value. It is evident in Figure A-6 that, at the highest concentration level (Level IV), all the single pair results were quite close to the expected value.

In summary, the results for carbon tetrachloride do not indicate any major deficiency in the VOST method, except for the high blank values and their effect on results at the lowest concentration level. If these high blank values were due to the gas generation system, then high blank values might not be a problem in any field testing. However, if the high blanks somehow resulted from the sampling trains, further work would be needed to determine how trains should be cleaned and prepared prior to each test to minimize blank problems. Field tests of the VOST are planned for the near future, which may help resolve this question.

4.3 TRICHLOROETHYLENE

Results for trichloroethylene, given in Figure A-7 (blank corrected), show a much narrower range at all concentration levels than did the results for vinyl chloride or carbon tetrachloride. The extremes varied from 70% of the expected value (at Level I for combined pairs), up to slightly above 140% of the expected value (at Level IV for single pairs). These results appear to be quite good for this compound using the VOST method.

4.4 CHLOROBENZENE

Results for chlorobenzene, given in Figure A-8 (blank corrected), are not as narrow as for trichloroethylene, but do show decreasing variability with increasing concentration levels. Again, data at the lowest concentration level showed the greatest deviation from the expected value, ranging from 36% up to 173% of the expected value. However, at the next higher concentration level (Level II), data for combined pairs ranged from 88% to about 140% of the expected value. At Level III, results for the single pairs were about the same, ranging from 70% to about 140% of the expected value. As is evident in Figure A-8, the range at the highest level was very narrow.

4.5 STABILITY DATA

One other objective of this project was to determine how long the Tenax traps might be stored after use, prior to analysis. This was investigated by preparing five, 84-ng standards (traps) at the start of the project, storing them at room temperature, and then analyzing each one in a sequence spanning several days.

Results of the analysis of the stability standards are presented in Table A-4. These data again show considerable variability for vinyl chloride and carbon tetrachloride, but do not seem to indicate any serious degradation or losses over the time period of about 2-1/2 weeks. However, the results for trichloroethylene and chlorobenzene do show some decrease over that time. A prudent conclusion is that traps should be analyzed within 2 weeks after samples are collected.

4.6 SUMMARY AND INTERPRETATION OF RESULTS

The preceding sections have shown that, at the two lowest concentration levels, the results for combined pairs of traps might range from 38 to 173% of the expected value (excluding higher values for carbon tetrachloride at the lowest level, which were not blank corrected). However, the data presented earlier in Table A-3 show that if three trains (or three runs) are used, the average for combined pairs may range from 48% up to 146% of the expected value. At the two highest concentration levels, the average for several pairs analyzed individually ranged from 70% up to 142% of the expected value (excluding a 43% average value for vinyl chloride at the highest concentration level where it appears that breakthrough occurred).

If one assumes, for simplicity of number, that the average value from three tests may span a range of 50 to 150%, it is possible to determine the implications on a subsequent calculation of DRE based on that range, as explained in the two scenarios given below.

In the first scenario, one may be trying to determine DRE for an incinerator that is actually achieving 99.999% for a POHC present in the waste at the low concentration of 100 ppm. As mentioned earlier, the approximate resulting true concentration of that POHC in the stack effluent would be about 0.1 ng/L. If this gas is sampled over a 2-hr period using 5 pairs of traps each time, at 20 min each pair and a flow of 1-L/min, the results from combining 5 pairs should be 10 ng. However, if the average for three tests (three runs) at this low concentration might range from 50 to 150%, the reported value would be between 5 and 15 ng. As a result, the computed DRE would be:

Average amount detected	Computed DRE (%)
5	99.9995
10	99.9990
15	99.9985

TABLE A-4. STABILITY STANDARDS (84-ng standards prepared on 4/24/82)

Date analyzed	Time interval after preparation (days)	Amount detected (ng)							
		Vinyl-chloride	Percent difference	Carbon tetrachloride	Percent difference	Trichloro-ethylene	Percent difference	Chloro-benzene	Percent difference
5/4/82	10	120	+43	48	-43	68	-19	75	-11
5/5/82	11	130	+55	68	-19	80	-4.8	87	+3.6
5/7/82	13	90	+7.1	93	+11	73	-13	79	-5.9
5/7/82	13	140	+67	89	+5.9	66	-21	67	-20
5/11/82	17	86	+2.3	58	-31	51	-39	48	-43

In this first scenario it is clear that the sampling/analysis method does allow an accurate determination of DRE, and minimizes the need to report a DRE value as "greater than" 99.99% when it is actually achieving 99.999%.

As a second scenario, the situation might be that the waste again contains 100 ppm of another volatile POHC, but the incinerator is actually achieving a DRE of 99.99%. In this case, the amount of POHC present from combining 5 pairs of traps should be 100 ng. Since the average for three tests at this level may again range from 50 to 150% of the true value, the reported value might be as low as 50 ng or as high as 150 ng (i.e., 100 ng ± 50). As a result, the computed DRE would be:

Average amount detected	Computed DRE (%)
50	99.995
100	99.990
150	99.985

From the above, it can be concluded that:

- The sampling/analyses method does provide assurance that the computed DRE is accurate to the same decimal place as the true DRE, even if the true DRE is as high as 99.999%.

- The computed DRE could be as low as 99.985% for an incinerator that is actually achieving 99.99%.

This second conclusion is vitally important since current regulations stipulate a DRE of 99.99%. Data obtained in this project make it appear unlikely that a computed DRE would be below 99.985% for an incinerator that is actually achieving 99.99%, if the computation is based on the average of three tests.

SECTION 5.0

CONCLUSIONS AND RECOMMENDATIONS

The conclusions and recommendations based on this evaluation of the VOST are presented below. Some of the conclusions are preliminary and could change upon further evaluation of the VOST. We also expect that the precision and accuracy of the method would improve during further evaluation.

5.1 CONCLUSIONS

- This laboratory evaluation demonstrates that the overall concept for the VOST is valid, and that combining several pairs of traps onto one pair of traps for analysis is advantageous when the POHCs are present at low levels.

- Results of the laboratory evaluation indicate that a reported value may be as low as 46% or as high as 146% of the expected value (based on the average of three runs when several pairs from each sampling train are combined onto one pair).

- For an incinerator that is achieving a DRE of 99.999% (100 ppm concentration of the POHC in the waste), the VOST method does permit determination of DRE to the third decimal place, but with results that could range from as low as 99.9985 to as high as 99.9995.

- The VOST method does overcome the problem of reporting a DRE value as > 99.99% for an incinerator which is actually achieving 99.999%.

- The VOST method does not ensure that DRE results can always be accurately computed to the third decimal place. In fact, if an incinerator is actually achieving a DRE of 99.99%, the average results reported for three tests could have a deviation of 99.99 ± 0.005%.

- In this evaluation, results for vinyl chloride and carbon tetrachloride show the most variability, especially at lower concentrations.

- The presence of HCl in the gas being sampled did not appear to have any serious affect on the VOST results.

- The problem of analyzing wet traps can be satisfactorily overcome by desorbing the contents of the sample collection traps into a purge-trap-desorb GC/MS analytical system.

5.2 RECOMMENDATIONS

- In this project, blank values for carbon tetrachloride were large compared to the lowest concentration level, and must be investigated further in order to determine if the above conclusions are still valid for this compound at low concentration levels.

- Samples obtained by the VOST method should be analyzed within 2 weeks.

- Three separate tests by the VOST method should be carried out, using the average to quantify emissions and compute DRE.

- Separate traps (blanks) should be exposed to air in the field in order to determine the level of compounds on the traps due to adsorption of the compounds during handling of the traps.

- The VOST method needs to be tested in the field.

- Some modifications of the VOST have been identified to minimize leak-check problems and breakage of the glass traps, and are under development for use in the field. The modifications include techniques of preventing contamination of the outside surfaces of the traps which might affect the analysis results.

- More extensive evaluation of the VOST method would be very useful to improve and possibly simplify the procedures and to reduce the variability in the results.

SECTION 6.0

TABULATION OF RESULTS FOR RUNS 2 THROUGH 10

This section contains a tabulation of the results for Runs 2 through 10 of the VOST testing. The results are presented in Tables A-5 through A-13, respectively. Run 1 was an exploratory run to check out procedures, and no results are reported for Run 1.

TABLE A-5. RESULTS FOR RUN NO. 2 (BLANK) ON 4/29/82

	Expected value (ng)	Amount detected (ng)[a]			
		Vinyl chloride	Carbon tetra-chloride	Trichloro-ethylene	Chloro-benzene
Train A pairs					
0 A1		-- Note: No single pairs were analyzed --			
0 A2					
0 A3					
0 A4	0	5.4	< 0.5	2.3	8.0
0 A5					
0 A6					
Train B pairs					
0 B1					
0 B2					
0 B3					
0 B4	0	4.8	< 0.5	2.5	6.4
0 B5					
0 B6					
Train C pairs					
0 C1		---- No Train C samples were analyzed ----			
0 C2					
0 C3					
0 C4					
0 C5					
0 C6					

[a] Amounts calculated based on average response factor determined from all standards (response factor for VC was based on analyzing standards on Tenax/charcoal traps; the other compounds were based on analyzing standards on Tenax traps).

TABLE A-6. RESULTS FROM RUN NO. 3, ON 4/30/82

	Expected value (ng)	Amount, in ng[a] (percent of expected value)							
		Vinyl chloride			Carbon tetrachloride		Trichloroethylene		Chlorobenzene	
		Measured value	Blank corrected value[b]	Desorb/adsorb corrected value[c]	Measured value	Blank corrected value[b]	Measured value	Blank corrected value[b]	Measured value	Blank corrected value[b]
Train A pairs										
III A1	183	220	220(120%)	-	226	222(121%)	191	190(104%)	171	171(93%)
III A2										
III A3										
III A4										
III A5										
III A6										
Train B pairs										
III B1	180	180	180(100%)	-	131	127(71%)	213	212(118%)	181	181(100%)
III B2										
III B3	178	190	190(107%)	-	150	146(82%)	210	209(117%)	241	241(135%)
III B4										
III B5	181	320	320(177%)	-	149	145(80%)	210	209(115%)	236	236(130%)
III B6										
Train C pairs										
III C1	211	350	350(166%)	-	88	84(40%)	217	216(102%)	Lost	- -
III C2	209	330	330(158%)	-	79	75(36%)	206	205(98%)	153	153(83%)
III C3										
III C4	207	330	330(159%)	-	160	156(75%)	227	226(109%)	241	241(116%)
III C5										
III C6										

[a] Amount calculated based on average response factor determined from all standards (response factor for vinyl chloride was based on analyzing standards on tenax/charcoal traps; the other compounds were based on analyzing standards on tenax traps).

[b] Blank corrections are based on data in Table A-2.

[c] Corrected value, for sevreral pairs that were desorbed onto one pair, was based on 49% transfer efficiency for vinyl chloride (other three compounds were not corrected because efficiences were 73, 89, and 98%, respectively).

TABLE A-7. RESULTS FROM RUN NO. 4, ON 5/4/82

	Expected value (ng)	Amount, in ng[a] (percent of expected value)								
		Vinyl chloride			Carbon tetrachloride		Trichloroethylene		Chlorobenzene	
		Measured value	Blank corrected value[b]	Desorb/adsorb corrected value[c]	Measured value	Blank corrected value[b]	Measured value	Blank corrected value[b]	Measured value	Blank corrected value[b]
Train A pairs										
I A1										
I A2	1.9	1.6	1.6(84%)	-	3.2(168%)	d	2.6	1.5(79%)	2.0	1.8(95%)
I A3										
I A4										
I A5	7.5	7.3	5.3	10.8(144%)	13(173%)	d	9.0	5.4(72%)	18	13(173%)
I A6										
Train B pairs										
I B1	1.9	1.3	1.3(68%)	-	5.1(268%)	d	2.6	1.5(79%)	2.0	1.8(95%)
I B2										
I B3										
I B4	9.7	6.0	3.5	7.1(74%)	10(103%)	d	16	11.5(119%)	10	3.5(36%)
I B5										
I B6										
Train C pairs										
I C1										
I C2										
I C3										
I C4	10.0	8.6	6.1	12.4(124%)	25(250%)	d	14	9.5(95%)	18	12(120%)
I C5										
I C6										

[a] Amounts calculated based on average response factor determined from all standards (response factor for vinyl chloride was based on analyzing standards on tenax/charcoal traps; the other compounds were based on analyzing standards on tenax traps).

[b] Blank corrections are based on data in Table A-2.

[c] Corrected value, for several pairs that were desorbed onto one pair, was based on 49% transfer efficiency for vinyl chloride (other three compounds were not corrected because efficiencies were 73, 89, and 98%, respectively).

[d] Data were not blank corrected because correction was large relative to measured value and would, in several cases, have resulted in negative values.

TABLE A-8. RESULTS FROM RUN NO. 5, ON 5/5/82

	Expected value (ng)	Amount, in ng[a] (percent of expected value)								
		Vinyl chloride			Carbon tetrachloride		Trichloroethylene		Chlorobenzene	
		Measured value	Blank corrected value[b]	Desorb/adsorb corrected value[c]	Measured value	Blank corrected value[b]	Measured value	Blank corrected value[b]	Measured value	Blank corrected value[b]
Train A pairs										
II A1										
II A2	19	13	13(68%)		13	9(47%)	24	23(121%)	30	30(158%)
II A3										
II A4										
II A5	76	18	16	33(43%)	80	53(70%)	86	82(108%)	100	95(125%)
II A6										
Train B pairs										
II B1										
II B2	21	12	12(57%)		10	6(29%)	22	21(100%)	29	29(138%)
II B3										
II B4										
II B5	78	18	16	33(42%)	99	72(92%)	87	83(106%)	112	107(137%)
II B6										
Train C pairs										
II C1										
II C2	17	12	12(71%)		15	11(65%)	23	22(129%)	29	29(171%)
II C3										
II C4										
II C5	78	24	22	45(58%)	105	78(100%)	89	85(109%)	107	102(131%)
II C6										

[a] Amounts calculated based on average response factor determined from all standards (response factor for vinyl chloride was based on analyzing standards on tenax/charcoal traps; the other compounds were based on analyzing standards on tenax traps).

[b] Blank corrections are based on data in Table A-2.

[c] Corrected value, for several pairs that were desorbed onto one pair, was based on 49% transfer efficiency for vinyl chloride (other three compounds were not corrected because efficiencies were 73, 89, and 98%, respectively).

TABLE A-9. RESULTS FROM RUN NO. 6, ON 5/6/82

	Expected value (ng)	Amount, in ng[a] (percent of expected value)								
		Vinyl chloride			Carbon tetrachloride		Trichloroethylene		Chlorobenzene	
		Measured value	Blank corrected value[b]	Desorb/adsorb corrected value[c]	Measured value	Blank corrected value[b]	Measured value	Blank corrected value[b]	Measured value	Blank corrected value[b]
Train A pairs										
IV A1										
IV A2	1,850	820	820(44%)	-	2,450	2,450(132%)	2,670	2,670(144%)	2,120	2,120(115%)
IV A3	1,870	950	950(51%)	-	1,710	1,710(91%)	2,440	2,440(130%)	2,070	2,070(111%)
IV A4										
IV A5										
IV A6										
Condensate	-	< 0.5			< 0.5		0.8		< 0.5	
Train B pairs										
IV B1										
IV B2	1,970	780	780(40%)	-	2,090	2,090(106%)	2,550	2,550(129%)	1,740	1,740(88%)
IV B3	2,100	910	910(43%)	-	2,220	2,220(106%)	2,580	2,580(123%)	2,040	2,040(97%)
IV B4										
IV B5										
IV B6										
Train C pairs										
IV C1										
IV C2	2,120	850	850(40%)	-	2,380	2,380(112%)	2,930	2,930(138%)	2,280	2,280(108%)
IV C3	2,240	940	940(42%)	-	2,220	2,220(99%)	2,770	2,770(124%)	2,040	2,040(91%)
IV C4										
IV C5										
IV C6										

[a] Amounts calculated based on average response factor determined from all standards (response factor for vinyl chloride was based on analyzing standards on tenax/traps; the other compounds were based on analyzing standards on tenax traps).

[b] Blank corrections are based on data in Table A-2.

[c] Corrected value, for several pairs that were desorbed onto one pair, was based on 49% transfer efficiency for vinyl chloride (other three compounds were not corrected because efficiencies were 73, 89, and 98%, respectively).

TABLE A-10. RESULTS FOR RUN NO. 7 (BLANK) ON 5/7/82

	Expected value (ng)	Amount detected (ng)[a]			
		Vinyl chloride	Carbon tetra-chloride	Trichloro-ethylene	Chloro-benzene
Train A pairs					
0 A1					
0 A2					
0 A3	0	4.7	35	5.0	8.1
0 A4					
0 A5					
0 A6	0	< 0.5	12.5	0.7	0.8
Train B pairs					
0 B1					
0 B2					
0 B3	0	1.1	49	6.6	10.0
0 B4					
0 B5					
0 B6	0	< 0.5	3.6	0.2	0.6
Train C pairs					
0 C1					
0 C2					
0 C3	0	Lost back T/C	17	6.3	4.0
0 C4					
0 C5					
0 C6	0	< 0.5	3.5	< 0.5	< 0.5

[a] Amounts calculated based on average response factor determined from all standards (response factor for vinyl chloride was based on analyzing standards on Tenax/charcoal traps; the other compounds were based on analyzing standards on Tenax traps).

TABLE A-11. RESULTS FROM RUN NO. 8, ON 5/10/82

	Expected value (ng)	Amount, in ng[a] (percent of expected value)								
		Vinyl chloride			Carbon tetrachloride		Trichloroethylene		Chlorobenzene	
		Measured value	Blank corrected value[b]	Desorb/adsorb corrected value[c]	Measured value	Blank corrected value[b]	Measured value	Blank corrected value[b]	Measured value	Blank corrected value[b]
Train A pairs										
II A1, II A2, II A3, II A4	75	59	57	116(155%)	154	127(169%)	83	79(105%)	98	93(124%)
II A5, II A6	19	14	14(74%)	-	15	11(58%)	25	24(126%)	21	21(111%)
Train B pairs										
II B1, II B2, II B3, II B4	74	52	50	102(138%)	112	85(115%)	87	83(112%)	95	90(122%)
II B5	21	20	20(95%)	-	19	15(71%)	23	22(105%)	20	20(95%)
II B6	19	16	16(84%)	-	-Lost front Tenax-		-Lost front Tenax-		-Lost front Tenax-	
Train C pairs										
II C1, II C2, II C3, II C4	87	64	62	126(145%)	82	55(63%)	92	88(101%)	96	91(105%)
II C5, II C6	22	16	16(73%)	-	11	7(32%)	25	24(109%)	21	21(95%)

[a] Amounts calculated based on average response factor determined from all standards (response factor for vinyl chloride was based on analyzing standards on tenax/charcoal traps; the other compounds were based on analyzing standards on tenax traps).

[b] Blank corrections are based on data in Table A-2.

[c] Corrected value, for several pairs that were desorbed onto one pair, was based on 49% transfer efficiency for vinyl chloride (other three compounds were not corrected because efficiencies were 73, 89, and 98%, respectively).

TABLE A-12. RESULTS FROM RUN NO. 9, ON 5/11/82

	Expected value (ng)	Amount, in ng[a] (percent of expected value)								
		Vinyl chloride			Carbon tetrachloride		Trichloroethylene		Chlorobenzene	
		Measured value	Blank corrected value[b]	Desorb/adsorb corrected value[c]	Measured value	Blank corrected value[b]	Measured value	Blank corrected value[b]	Measured value	Blank corrected value[b]
Train A pairs										
II A1-HCl, II A2-HCl, II A3-HCl, II A4-HCl	74	44	42	86(116%)	105	78(105%)	75	71(96%)	83	78(105%)
II A5-HCl, II A6-HCl	19	12	12(63%)	-	8.7	4.6(24%)	21	20(105%)	19	19(100%)
Train B pairs										
II B1-HCl, II B2-HCl, II B3-HCl, II B4-HCl	69	30	28	57(83%)	109	82(119%)	73	69(100%)	65	60(87%)
II B5-HCl, II B6-HCl	19	26	26(137%)	-	14	10(53%)	19	18(95%)	17	17(89%)
Train C pairs										
II C1-HCl, II C2-HCl, II C3-HCl, II C4-HCl	87	22	20	41(47%)	121	94(108%)	107	103(118%)	90	85(98%)
II C5-HCl, II C6-HCl	21	19	19(90%)	-	13	9(43%)	20	19(90%)	18	18(86%)

[a] Amounts calculated based on average response factor determined from all standards (response factor for vinyl chloride was based on analyzing standards on tenax/charcoal traps; the other compounds were based on analyzing standards on tenax traps).

[b] Blank corrections are based on data in Table A-2.

[c] Corrected value, for several pairs that were desorbed onto one pair, was based on 49% transfer efficiency for vinyl chloride (other three compounds were not corrected because efficiencies were 73, 89, and 98%, respectively).

TABLE A-13. RESULTS FOR RUN NO. 10, (BLANK) ON 5/28/82[b]

	Expected value (ng)	Amount detected (ng)[a]			
		Vinyl chloride	Carbon tetra-chloride	Trichloro-ethylene	Chloro-benzene
Train A pairs					
0 A1	0	< 0.5	1.2	3.4	< 0.5
0 A2					
0 A3					
0 A4	0	< 0.5	53	4.8	1.8
0 A5					
0 A6					
Train B pairs					
0 B1	0	< 0.5	3.7	< 0.5	< 0.5
0 B2					
0 B3					
0 B4	0	< 0.5	50	2.2	3.6
0 B5					
0 B6					
Train C pairs					
0 C1	0	< 0.5	< 0.5	2.0	< 0.5
0 C2					
0 C3					
0 C4	0	< 0.5	54	3.0	6.2
0 C5					
0 C6					

[a] Amounts calculated based on average response factor determined from all standards (response factor for VC was based on analyzing standards on Tenax/charcoal traps; the other compounds were based on analyzing standards on Tenax traps).

[b] Gas generation system and sampling trains were purged with vapor from liquid N_2 tank at ambient temperature for 24 hr prior to test.

APPENDIX B

SAMPLING METHODS AND ANALYTICAL PROCEDURES

SECTION 1.0

INTRODUCTION

This appendix describes the field sampling procedures and the field and laboratory analytical methods used for testing hazardous waste incinerators. The objective of the appendix is to provide full documentation of the sampling and analysis methods that were used to generate data from the eight hazardous waste incinerator sites described in the main body of the report and Appendices C through J.

The appendix is divided into two major sections. Section 2.0 describes the field sampling procedures and field analysis methods that were used at each of the eight sites. Section 3.0 describes all aspects of laboratory chemical analyses that were conducted during the program.

SECTION 2.0

FIELD SAMPLING AND FIELD ANALYSIS METHODS

The field sampling procedures and analysis methods which were used for testing hazardous waste incinerators are described in this section. These procedures were used to acquire samples from all inputs to, and outputs from, the incineration systems in order to fully evaluate those systems. The details of the sampling techniques are described for the sampling of the waste feed streams, ash discharge, scrubber influents and effluents (where applicable), and stack effluent. In addition, the details of the on-site analysis of specific inorganic and organic gases are described.

Standard EPA Reference Methods and EPA recommended methods were employed wherever possible. However, due to the comprehensive nature of the test program, new and developmental methods were used in some situations to fill the sampling and analysis requirements. Research into adequate methods of sampling and analysis was necessary throughout the test program, resulting in the evolution of several new procedures.

The data obtained on this program were used to determine the Destruction and Removal Efficiency (DRE) for each Principal Organic Hazardous Constituent (POHC). Therefore, the identification and quantification of specific POHCs in the waste and in stack emissions were critical aspects of the sampling and analysis. Quantitative collection and recovery of compounds present in low concentrations were also critical considerations. The methods of sampling and analysis were chosen based on these considerations.

This section has eight subsections describing the field sampling and analyses procedures. A general description of each procedure and variations of the procedures used at specific test sites are provided. The following sections are included:

Sampling of Stack Effluent Using Modified Method 5
Volatile Organic Sampling
Grab Sampling
Specific Absorption Trains
Continuous Monitoring
Spiking of Waste Feeds
Process Monitoring
Visible Emission Evaluation
Routine Analyses of Waste Feeds and Ash

2.1 SAMPLING OF STACK GAS EFFLUENT USING MODIFIED METHOD 5

2.1.1 Introduction

A Modified Method 5 (MM5) sampling train was chosen as the best available comprehensive sampling system for this test program. The MM5 train was used to collect samples for determining particle concentration, hydrogen chloride (HCl) concentration, semivolatile POHC emissions, and emissions of semivolatile products of incomplete combustion (PICs). Particulate samples collected in the train were analyzed for metals at some test sites.

The sampling equipment was operated using isokinetic sampling techniques to ensure the gas samples collected were representative of the total source emissions. For cyclic or batch processes, the sample was collected over a sufficient length of time to ensure a representative average sample. The use and operation of a MM5 sampling train for measurement of emissions from hazardous waste incinerators paralleled the procedures specified in EPA Methods 1 through 5 for collection of particulate emissions. The specific modifications, exceptions, and special sampling techniques are discussed below for five specific aspects of the testing: pretest preparation, preliminary on-site activities, assembly of the MM5 train, sampling, and on-site analyses.

2.1.2 Pretest Preparation

2.1.2.1 Preparation of Glassware--

The glassware associated with the sampling train was cleaned using the following procedure. All glassware was first cleaned with hot, soapy water. If encrusted materials remained on the glass surfaces, the glassware was dipped into an acid bath first and then washed with soapy water. This washing was followed by rinses with tap water and then deionized water. Distilled-in-glass methanol was used as the final rinse. The glassware was dried thoroughly in a clean oven at ≧ 110°C and then capped with methanol-cleaned aluminum foil. The foil caps remained on the glassware until the component was used in the assembly of the sampling train.

2.1.2.2 Preparation of Filters and Reagents--

The 10-cm (4-in.) high-efficiency glass fiber filters were prepared and tared according to EPA Method 5 specifications. Glass petri dishes with aluminum weighing boat inserts were used as the shipping and storage containers for the filters. The petri dishes, rather than the filters, were labeled with a number, and the filters were kept in the containers at all times, except during sampling and weighing.

The reagents used in sampling and recovery were of higher purity than specified in EPA Method 5 in order to keep reagent background levels low. Double-distilled-in-glass water and 0.1 N potassium hydroxide (KOH), made with double-distilled water, were used in the sampling train impingers, as well as indicating silica gel (see Section 2.1.4). Fresh solutions were made prior to each test program. The double-distilled water was stored and transported to the field in a 4-L glass bottle. The KOH solution was stored and transported in a 500-mL Teflon bottle. During the assembly of the train, ground glass joints were lightly coated with Apeizon-L grease to prevent leaks.

Distilled-in-glass acetone (Burdick and Jackson) was the organic solvent used in the sample recovery. Natural bristle brushes properly sized and shaped were also used to brush out the probe and nozzle during recovery (see Section 2.1.5.3). At the test site, the acetone and double-distilled water were transferred to Teflon wash bottles for ease of handling during sample recovery.

2.1.2.3 XAD-2 Cleanup and Trap Preparation--

A batch (batch number was recorded in LRB) of XAD-2 adsorbent (~ 2,000 g) was placed into a continuous extraction column and washed successively with:

- One liter distilled water
- One liter 0.1 N sodium hydroxide
- One liter distilled water
- One liter 0.1 N hydrochloric acid
- One liter distilled water
- One liter methanol (2 times)

The XAD-2 was then Soxhlet-extracted 24 hr with methanol, followed by 24-hr Soxhlet extractions with acetonitrile, and methylene chloride. The XAD-2 was then placed into a container with a screw-cap top and dried in a vacuum oven at room temperature for several hours.* The container was immediately capped upon removal from the oven. The XAD-2 was stored under methanol in a tightly capped jar until it was loaded into the sampling cartridges.

2.1.3 Preliminary Test Site Activities

2.1.3.1 Preliminary Measurements--

The criteria for selection of sampling port locations and number, location of sampling points within a stack, and determination of moisture and molecular weight for the calculation of isokinetic sampling rates were identical to those outlined in EPA Methods 1 through 4.

Four of the eight test sites had saturated gas streams (Ross, Upjohn, Du Pont, and TWI). The required velocity traverse (EPA Method 2) was difficult to perform on a saturated stack. After the probe was inserted in the stack, the pitot lines filled with water. Normally, when this occurred, the line from the pitot tube was disconnected from the manometer and blown out with compressed air.

For the preliminary calculation of the dry molecular weight of the gas, a grab sample of stack gas was collected according to EPA Method 3. A Fyrite analyzer was used to analyze the gas for carbon dioxide (CO_2) and

* The XAD-2 was inadvertently heated to 110°C in the vacuum oven for 4 hr for the Plant B and Upjohn tests. XAD-2 starts to degrade above 120°C. The 110°C used caused the XAD-2 blank values to increase but did not cause any apparent problem with the POHC analysis.

oxygen (O_2). During each test run, a single-point integrated gas sample was collected in a leak-free Mylar bag as outlined in EPA Method 3. The gas was sampled at a constant rate throughout the MM5 test run sufficient to collect a minimum of 30 L. After each test run, the gas bag sample was analyzed for CO_2 and O_2 in the field laboratory using an Orsat analyzer.

2.1.3.2 Cyclonic Flow--

The presence or absence of cyclonic (tangential) flow at each MM5 sampling location was determined for every test site. Where cyclonic flow conditions occur, the effluent gas flows in a spiral motion up the stack, making the overall flow condition unacceptable for isokinetic sampling. The techniques used for this determination were identical to those outlined in EPA Method 1.

The absence of cyclonic flow was verified at six of the eight test sites. At American Cyanamid and Mitchell, after applying the null technique to each traverse point, the average rotation angle exceeded the recommended limits, indicating unacceptable cyclonic flow conditions. In these cases, temporary flow straighteners were fabricated and installed in each stack, at least two duct diameters upstream of the sampling ports. The straightening vanes used were designed according to the guidelines specified in "Techniques to Measure Volumetric Flow and Particulate Concentration in Stacks with Cyclonic Flow,"[1] with a cell size of D/4 and a length of D/2. After installation, another check for cyclonic flow showed that the flow straighteners had corrected the problem and the stack gas flow was essentially parallel to the stack walls.

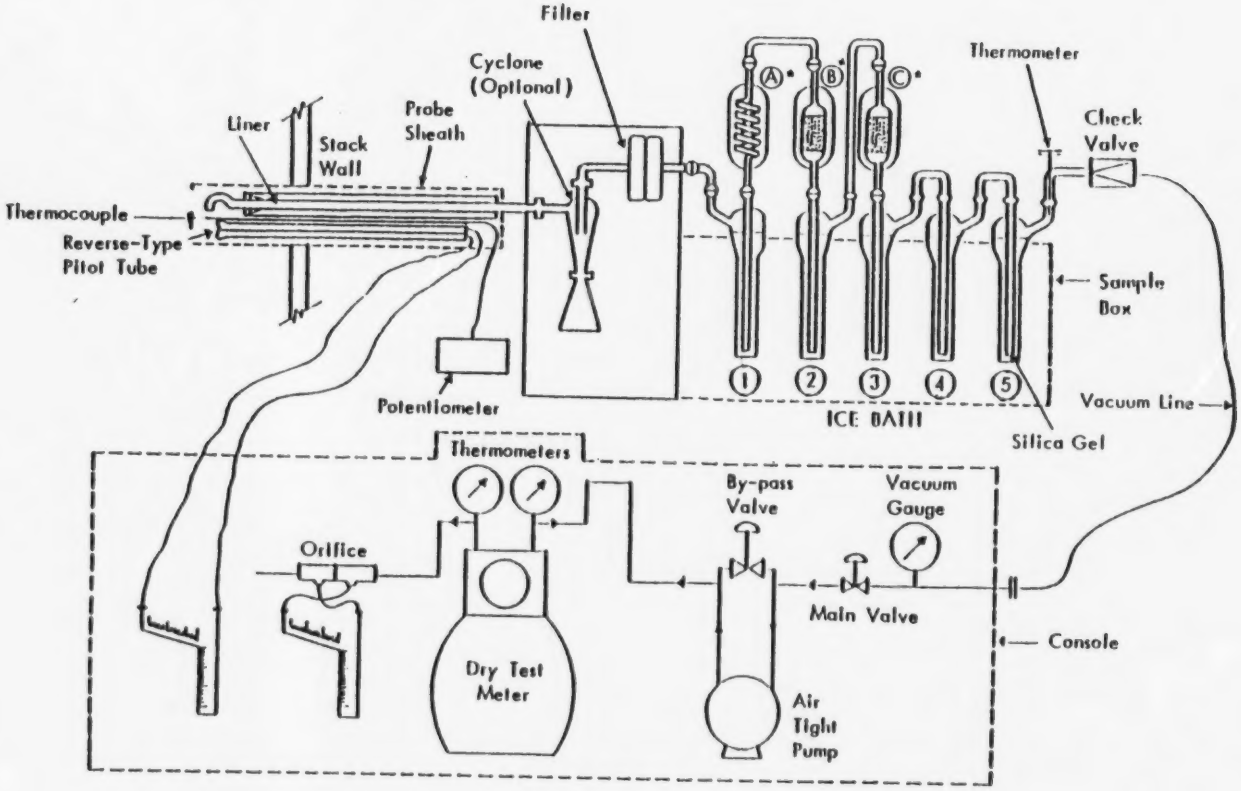
2.1.4 Assembly of Modified Method 5 Sampling Train

The MM5 sampling system is based upon the train designed for and employed in particulate sampling using EPA Method 5 methodology. The modified system is shown in Figure B-1. The modifications to the basic system for these tests included:

- A reversed impinger to knock out free water;
- A condenser to cool the gas stream;
- Water jacketed sorbent modules to collect semivolatile POHCs;
- A 4-L condensate collector to permit completing a traverse before emptying (in saturated stacks);
- Use of 0.1 N KOH in the impinger to collect acid gases; and
- The type and arrangement of the impingers in the train.

2.1.4.1 Sampling Probe and Nozzle--

The probe was constructed of medium-wall borosilicate or quartz glass tubing wrapped with heating wire and sheathed in a stainless-steel jacket. A suitable probe liner and probe length were selected for each test site. Before sampling began and during sample collection, the probe was heated to



① Modified Greenburg-Smith, Reversed, Empty
② Greenburg-Smith, 50 ml of Double Distilled In Glass H_2O
③ Greenburg-Smith, 100 ml of 0.1 N KOH
④ Modified Greenburg-Smith Empty
⑤ Modified Greenburg-Smith, SiO_2

Ⓐ Condenser
Ⓑ XAD Resin Cartridge #1
Ⓒ XAD Resin Cartridge #2
* Ice Water Jacket

Figure B-1. Modified Method 5 sampling train (MM5).

approximately 120° ± 14°C (250°F) in order to prevent condensation of stack gas in the probe. Quartz-lined sampling probes were necessary at Zapata, American Cyanamid, and Mitchell due to high stack gas temperatures (> 550°C).

The probe nozzle was of the button-hook or elbow design, fabricated from stainless steel and calibrated according to EPA Method 5 specifications. At each test site, the appropriate nozzle size was selected, based on the range of velocity heads measured, so that the calculated isokinetic sampling rate could be maintained. The selected nozzle was installed on the probe using a Teflon ferrule when stack temperatures were less than 260°C (500°F) and with an asbestos string gasket when temperatures were higher.

The probe, with nozzle attached, was marked with glass cloth tape to indicate the proper distance into the stack for each sampling point. Prior to being transferred to the sampling location, the probe assembly was rinsed with distilled-in-glass acetone in the field lab, and then capped with cleaned aluminum foil.

2.1.4.2 Cyclone and Filter--

To reduce contamination, a limited access area of the field lab was maintained. The sampling train was assembled in this designated clean area of the field lab. Activities not directly related to train preparation or sample recovery were done elsewhere. During preparation and assembly, all openings to the train where contamination could occur were covered with cleaned aluminum foil until just prior to assembly or start of sampling.

The first component assembled in the sample box was the cyclone and/or filter assemblies. In gas streams where the particulate concentration was expected to be heavy, or where water droplets were large, a glass cyclone with a collection flask was used, as shown in Figure B-1. The cyclone was placed between the probe and the filter holder to prevent overloading of the filter.

A sintered glass filter support was used to house the tared glass fiber filter, Teflon-coated gasket, and fritted glass filter back-up. The holder was loaded and assembled in the field lab with the aid of stainless steel foreceps. The cyclone was deleted from the train when minimal particulate loading was expected. In these cases, the gas passed from the probe directly to the high-efficiency filter.

Oversized heaters were installed in the filter compartment of the sample box in order to keep the filter dry while sampling. These heaters were especially important when sampling cool gas streams containing free droplets of water. The filter box was heated to near the upper temperature limit of 134°C (275°F), as specified in EPA Method 5, before sampling was started. To reduce the potential for filter back-up breakage, a support was added to the back half of the filter holder, as shown in Figure B-2.

2.1.4.3 XAD-2 Resin Cartridges--

Vaporous emissions of semivolatile POHCs were collected by the XAD-2 resin beds in the sampling train.

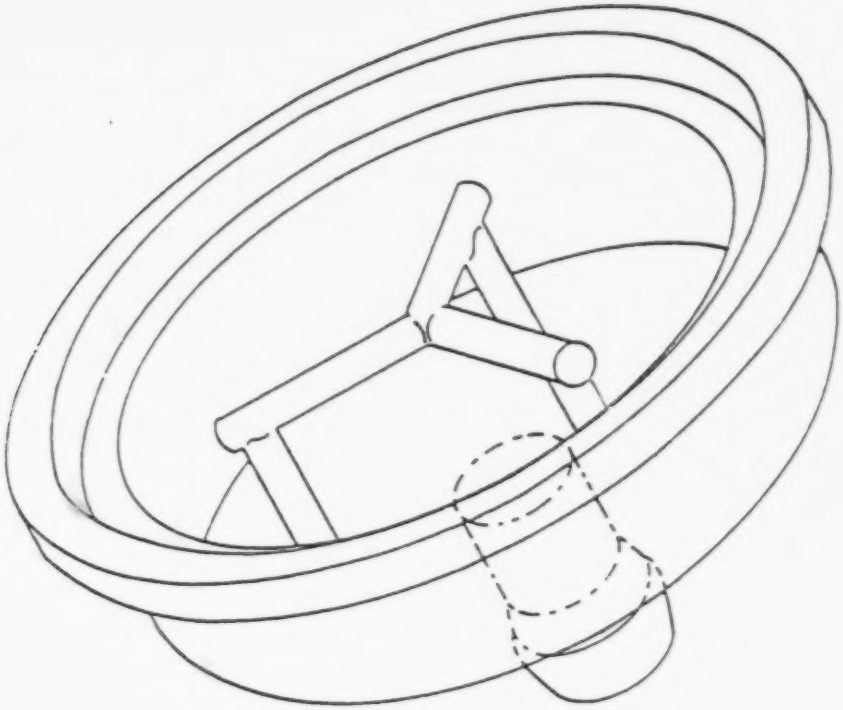


Figure B-2. Support for filter frit (back half of filter support).

Downstream of the heated filter, the sampled gas passed through an empty reversed impinger of the modified Greenburg-Smith design in order to retain excess water. The gas stream was cooled as it passed through a water-cooled condenser, mounted vertically atop the reversed impinger, before reaching the two sorbent modules packed with precleaned XAD-2 resin (see Figure B-1).

The recommended protocol for use of XAD-2 resins is outlined in the EPA Level 1 Procedures Manual. The sorbent resin used in the cartridges was precleaned, and its cleanliness was verified prior to use. The cartridges were packed in the analytical laboratory prior to shipping to the field.

The module that housed the sorbent trap was water-jacketed (see Figure B-3). Cold water from an ice bath surrounding the impingers was pumped through the jacket to maintain an outlet temperature of ≦ 16°C (60°F). All sorbent traps were wrapped in aluminum foil due to the possible sensitivity of potential analytes to ultraviolet light.

Downstream from the condenser the cooled sample gas and condensed vapor flowed through the first resin bed mounted vertically atop the second impinger of the sampling train. The condensate was collected in this impinger while the gas passed through the second XAD-2 cartridge. This trap was mounted similarly on the third impinger to ensure collection of all semivolatile POHCs in the gas stream.

2.1.4.4 Impingers--

Five impingers immersed in an ice bath were utilized as the condenser system of the sampling train to collect condensate and acidic gases (see Figure B-1). A light coat of Apiezon-L grease was used on the ground glass joints of the train components to prevent leakage.

The first impinger was reversed in order to knock out free water. The first XAD-2 cartridge was mounted on top of the second impinger. The condensed stack gas vapor percolated through the resin bed and was discharged into this impinger. The impinger was of the Greenburg-Smith design and contained 50 mL of double-distilled water prior to sampling. Due to the expected large volume of condensate, a volume of 50 mL was used instead of the recommended 100 mL. Oversized (4 L) condensate collectors were used when sampling saturated stacks instead of standard impingers 2 and 3 shown in Figure B-1.

The third impinger, connected to the outlet of the second sorbent module, incorporated a caustic solution in order to collect HCl and other acidic gases. One hundred milliliters (100 mL) of 0.1 N KOH was placed in the impinger (Greenburg-Smith design) prior to sampling. The fourth impinger was of the modified Greenburg-Smith design and left empty. Typically, the final impinger was filled with approximately 200 to 300 g of silica gel to ensure complete desiccation of the gas before entering the control console. The silica gel was weighed directly in its impinger prior to train assembly, and the total weight was recorded.

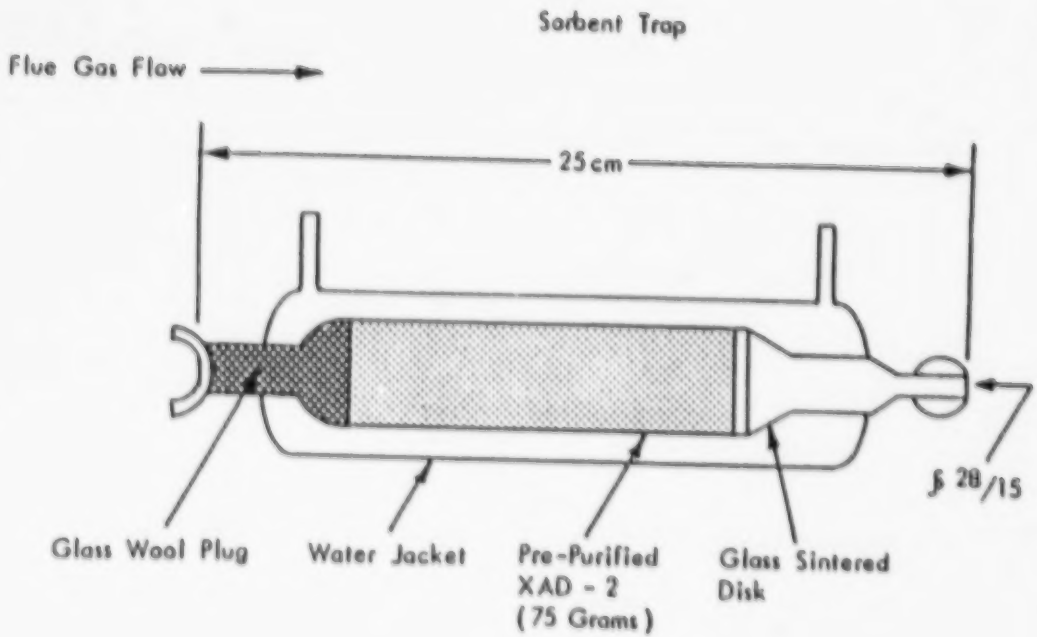


Figure B-3. Sorbent trap for Modified Method 5 train.

2.1.4.5 Train Control Equipment--

A schematic of the control console used with the train to collect the gas sample is shown in Figure B-1. The maintenance and calibration of the sampling equipment prior to testing followed the procedures outlined in EPA Method 5 including: probe nozzle diameter measurements; pitot tube, and dry gas meter calibrations; and dial and liquid-filled thermometers and thermocouple-potentiometer systems calibrations.

2.1.5 Sampling

2.1.5.1 Operation--

After assembly, the sampling train and probe were transferred from the field lab to the sampling location for a pretest checkout. Due to the increased number of ground glass connections, the train first had to be leak-checked without the probe. Standard EPA Method 5 methodology was used accordingly. The fitting at the inlet of the filter holder (or cyclone, if used) was sealed, and the sample box heating system was set at the operating temperature. The sample pump was turned on, and the dry gas meter was observed for at least 1 min for the existence of any appreciable flow. The train had to pass the EPA Method 5 standard leak test of less than 570 cc/min at 51 kPa or 4% of the sampling rate, whichever was less, to be acceptable.

When the leak test of the train was completed, the probe was connected to the train in order to leak check the entire system. The probe nozzle was plugged and the above procedure was repeated (≦ 570 cc/min at 51 kPa). In stacks where the gas temperature was above 260°C (500°F), an asbestos string gasket was used to install the nozzle on the probe. The sampling train was then leak checked, but the system with the probe attached was checked at a vacuum of 3.4 kPa, as described in EPA Method 5. Under no condition was a sampling test conducted with a leak rate in excess of 570 cc/min. In addition, the pitot tubes were leak tested according to EPA Method 2 procedures.

Crushed ice and cold water were placed around the impingers. The circulating water pump was turned on to supply water to chill the condenser and XAD-2 traps. Before positioning the probe at the first sampling point in the stack, the probe and sample box oven were allowed to heat to the operating temperature of 120 ± 14°C (250°F).

During the sampling run, standard EPA methodology for particulate sampling, EPA Method 5, was followed. The sampling rates were finely adjusted to obtain a sample at the desired isokinetic conditions. A volume of approximately 1,700 L (dry standard) was collected for each test run in a 2-1/2 to 3 hr sampling period at an average sampling rate of 14 L/min.

During the course of the sampling run, scheduled parameter checks were made on flow rate, volume, temperature, and pressures. These data, along with other data required on the data sheet, were recorded at least once at each sampling point. Sufficient ice was kept in the sample box to keep the impingers cool and to chill the condenser and sorbent traps. Periodic adjustments were made to keep the probe and sample box oven at the proper

temperature throughout the test run. Also, periodic checks on the manometer level and zero were necessary due to vibrations and ambient temperature changes.

At the conclusion of the sampling run, post-test leak checks were performed on the system. Again, the pitot lines were tested in order to validate the velocity head data. The probe and train assembly were leak checked according to the procedure described earlier, except that the leak check was conducted at a vacuum equal to or greater than the maximum value reached during the sampling run. When asbestos string gaskets were used, the sampling system with the probe attached was tested at 3.4 kPa. However, the train was checked separately at the maximum vacuum, or greater, reached during the sampling run. The test results were acceptable if the leak rate was ≦ 570 cc/min or 4% of the average sampling rate (whichever was less).

2.1.5.2 Exceptions--

Three of the test sites, Zapata, American Cyanamid, and Mitchell, did not utilize control equipment and operated with stack temperatures in the 650° to 800°C (1200° to 1470°F) range. These stacks were sampled by positioning all equipment at locations remote from the stack, with the exception of the EPA Method 5 sampling probe and sample box. During a test, the only crew member on the sampling platform was the probe pusher, who was protected by a thermal blanket and high temperature gloves. A standard stainless steel probe sheath was used for the EPA Method 5 train, and gas samples were collected using a quartz-lined probe. The nozzle was installed with an asbestos string gasket.

In addition, the incinerator at American Cyanamid was operated between 1 and 2-1/4 hr each day to burn the accumulated aniline waste. The length of the burn time was dependent upon the limited storage capacity for the aniline waste. Due to the short burn time, several testing factors were modified. Two MM5 sampling trains were operated simultaneously with each train traversing one stack diameter. Approximately 800 L (dry standard) of stack gas was collected in each train in 1 hr, although the isokinetic sampling rates were unique to each train. The samples were handled and analyzed separately. However, the calculated results were added together to characterize the total emissions.

2.1.5.3 Sample Recovery--

Proper cleanup procedure began as soon as the probe and sampling train were removed from the stack at the end of the sampling run. EPA Method 5 methodology for sample recovery was followed with the addition of procedures to recover the additional analytes from the modified components of the train. Burdick and Jackson distilled-in-glass acetone was the organic solvent used for cleanup. Clean Teflon wash bottles were used for all rinsings.

When the probe could be safely handled, all external particulate matter near the tip of the nozzle was wiped off. The probe was removed from the train and the mating joints of both the probe and the train, as well as the nozzle, were capped with solvent-rinsed aluminum foil to prevent contamination. Also, the outlet of the train was capped after disconnecting from the pump. The probe and train assemblies were then transferred to the field laboratory for sample recovery.

The system was inspected prior to and during disassembly. Any abnormal conditions were noted in the lab book. A brief summary of the treatment of each sample is shown in Table B-1. The sample recovery procedures are discussed below.

2.1.5.3.1 Probe--The sampling nozzle was removed and set aside for later recovery. A 500 mL socket flask was connected to the ball joint of the probe in order to collect the probe rinse. The probe was rinsed with three portions of acetone (Burdick and Jackson) while the entire length of the probe was brushed with a natural bristle brush. The probe was brushed at least three times or until no visible particulate was seen in the acetone.

When a glass cyclone was used, the cyclone and its collection flask were carefully rinsed out with acetone. If particulate was adhering to the glass, a natural hair brush was utilized to brush the sides of the cyclone or flask. All rinses were added to the probe rinse container. When a cyclone was omitted from the train, the connecting glassware from the probe to the filter holder (cyclone bypass) was rinsed with acetone and added to the probe rinse.

Using a small natural hair brush and Burdick and Jackson acetone, the nozzle was cleaned, collecting the rinsings in the 500 mL flask with the probe rinse. All brushes used were rinsed with Burdick and Jackson acetone and added to the probe rinse. The contents of the 500 mL flask were quantitatively transferred to container No. 1. The bottle was labeled appropriately. (See Section 2.1.5.4 for further details.)

2.1.5.3.2 Filter--The filter holder was carefully disassembled, taking care to keep the particulate matter on the filter from being disturbed. Using stainless steel tweezers, the filter was removed and placed in its original petri dish (container No. 2). Care was taken to avoid tearing the filter or losing particulate matter. Any particulate matter and/or filter fibers which adhered to the Teflon gasket were transferred to the aluminum dish in the petri dish with the aid of a sharp-edge blade or camel-hair brush. The petri dish was labeled and sealed. After removal of the filter the front-half of the filter housing was subjected to several rinsings with acetone. These rinsings were combined with the probe rinse. The back-half of the filter holder was set aside for later recovery.

2.1.5.3.3 XAD-2 resin cartridges--The condenser was removed and set aside for later recovery. The resin cartridges were removed one at a time, starting with the first cartridge atop the second impinger. The ends of the cartridge were capped off securely with aluminum foil which had been cleaned with methanol. The foil was further secured by wrapping a rubber band or wire around the neck of the ball joints. A label was affixed to the cartridge on the outside of the pretest foil wrap before placing the trap in a shipping container. (See Section 2.1.5.4 for further details.) The second sorbent module was removed and treated in the same manner as described above. The cartridges were iced at all times after recovery.

2.1.5.3.4 Condensate--The first impinger from the sample box was removed, and the ball joints were wiped clean with a Kimwipe. Without removing the impinger stem, the contents of the impinger (aqueous condensate)

TABLE B-1. SUMMARY OF SAMPLE RECOVERY[a]

Container No.	Contents description	Container type	Storage requirements
1	Front-half rinse including probe	1 L, glass	On ice
2	Filter	Glass petri dish with aluminum weighing pan	Dry; upright
3 & 4	XAD-2 resin cartridges	(Cartridge)	On ice
5	Condensate; contents of first two impingers	1 L, glass (4 L glass if saturated stack)	On ice
6	Cl aliquot; this sample is ≅ 60 mL of the sample in container No. 5 used for chloride analysis	60 mL, polypropylene	Dry
7	KOH; contents of impinger Nos. 3 and 4	1 L, Teflon	Dry
8	Filter blank	Glass petri dish with aluminum weighing pan	Dry; upright
9	Acetone blank	1 L, glass	On ice
10	KOH blank	1 L, Teflon	Dry
11	XAD-2 resin blank	(Cartridge)	On ice

[a] Computer generated labels and sample numbers were assigned to each sample. However, for ease of explanation, container numbers have been used here.

were poured into a 250 mL graduated cylinder. The volume was recorded on the sample recovery data sheet to the nearest milliliter. This solution was then quantitatively transferred to container No. 5. The impinger was set aside for subsequent rinsings. The content of the second impinger was recovered in the same manner and added to the same sample container (container No. 5).

Using a large-mouth glass funnel as an aid, the back-half of the filter, the condenser, impinger Nos. 1 and 2, and all connecting glassware in front of the third impinger were rinsed with small volumes of double-distilled water. Only one rinse of the glassware was necessary. All rinses were collected into a 250 mL graduated cylinder and the volume measured. This volume was recorded on the recovery data sheet. These rinses were combined with the preceding condensate samples.

Care was taken to completely contact the interior surfaces of the train with each rinse to quantitatively remove the analyte material. Rinsing volumes of each solvent used for each component were recorded to allow the accurate determination of solvent background contributions.

With the cap tightly closed, container No. 5's contents were mixed thoroughly. An aliquot or subsample of approximately 60 mL was placed in a 60 mL polypropylene sample bottle (container No. 6). Each sample was labeled appropriately and placed in the designated shipping container.

2.1.5.3.5 Potassium hydroxide (KOH)--The third impinger with the KOH solution, as well as the dry fourth impinger, were removed from the sample box. The ball joints were wiped clean with a Kimwipe. Recovery of the contents in impinger Nos. 3 and 4 was identical to the procedure followed in the recovery of the condensate, except that a Teflon sample bottle (container No. 7) was used as the sample container. The two impingers and the connecting "U"-tube were rinsed with double-distilled water, and the rinses were added to the sample container. The solution and rinse volumes were recorded on the recovery data sheet. The sample bottle was labeled and placed in the appropriate shipping container.

2.1.5.3.6 Silica gel--The fifth impinger was removed from the sample box and wiped clean. The color of the indicating silica gel was noted to determine if it had been completely spent. The condition was recorded on the data sheet. The silica gel in its impinger was weighed in the same manner as when it was tared. This weight was recorded on the recovery sheet. If spent, the reagent was discarded. No further analysis was made on the silica gel.

2.1.5.4 Field Blanks--

The collection of field blanks was mandatory to indicate the cleanliness of all sample handling phases and to determine the contribution of reagent background levels. Blanks of the acetone, filters, resin cartridges, and KOH solution were collected and treated in the same manner as samples. During a sampling program, a minimum of two samples of each reagent were taken as blanks.

The resin cartridge and filter blank were exposed to the same field laboratory environment for the same time intervals as the sample filter and sorbent resin. The exposed filter was returned to its original container and labeled as the filter blank. Similarly, the exposed resin trap was recapped with foil and appropriately labeled. A sample of acetone was dispensed from the wash bottle into a sample container (container No. 9) for each solvent lot number used in recovery. The volume of solvent collected was approximately equal to the solvent volumes used during recovery of the front-half of the train. A 100 mL sample was taken from the KOH solution and transferred into a labeled Teflon sample container.

2.1.5.5 Calculations--

The moisture content of the sample gas stream was calculated, except for saturated stacks, from the total condensate volume, plus any increase in the KOH solution volume, and the moisture collected in the silica gel impinger. The integrated gas bag sample, collected in a Mylar bag during the MM5 sampling period, was analyzed by an Orsat analyzer to determine levels of O_2 and CO_2. The molecular weight of the gas stream was then calculated. Using the calculations outlined in EPA Method 5, the percent isokinetic was determined for the MM5 test run. The results were acceptable, and the test run considered valid if the isokinetic percentage was greater than or equal to 90%, but less than or equal to 110% ($90\% \leq I \leq 110\%$).

2.1.5.6 Sample Handling and Shipping--

As stated previously, the manner in which the samples were handled and shipped affected the reliability of the analysis. After recovery, the samples were packaged and stored in the field laboratory to prevent sample loss and to maintain sample integrity. At the end of each test program, the shipping containers with the samples were loaded onto the sampling equipment truck and transported back to the analytical lab.

All liquid samples from the recovery of the sampling train (probe rinse, condensate, and KOH) were transferred to air-tight glass or Teflon sample bottles with Teflon-lined lids. Immediately after the transferral of the sample, a preprinted label, as described in Section 2.3.6.1, was affixed to the sample container. The container was capped tightly to prevent loss of material, and the cap was taped for extra protection. The height of the liquid level was marked on the exterior of the sample bottle. This marking allowed any losses of sample material during handling and shipping to be detected and noted.

To further reduce sample loss prior to analysis and to protect the sample during shipping, each sample bottle was placed in a polyethylene bag and secured with a twist tie. The wrapped bottle was placed in its appropriate storage and shipping container. The acetone rinses, including the blank samples, and the condensate samples were placed in coolers which served as refrigerated storage containers as well as shipping containers. The coolers were kept at 4° to 6°C (39° to 43°F) using ice in sealed bags. Since the KOH samples and the aliquots from the condensate samples did not need to be kept cold, these samples were handled as described above and placed in a cooler without ice. A separate cooler was used for each type of sample.

The filters and resin cartridges required special handling and packaging for shipping. After sampling, the particulate filters were recovered and returned to their original petri dishes. The blank filters were exposed to the field lab environment and then returned to their original container. Each petri dish was taped shut with masking tape. The sample identification label was placed on the top center of each dish, adding the filter number to the label. Each petri dish was carefully placed in a polyethylene bag and sealed with a twist tie. Care was taken to ensure that the filters remained upright during storage and shipping. The filter samples were stacked in a rigid container, such as a cardboard box, with packing material arranged around and between each wrapped petri dish.

After removing the cartridge from the train, the ends of the resin cartridge were capped with solvent-rinsed foil and secured. A sample identification label was affixed to the aluminum foil covering on the cartridge. The entire cartridge was wrapped in a bubble pack and then sealed inside a polyethylene bag. A duplicate sample label for the cartridge was attached to the outside of the bag. The cartridges were stored and shipped in a cooler kept at 4° to 6°C (39° to 43°F) at all times using ice in sealed bags.

A log of all samples collected was kept in the field as the samples were generated and/or recovered. The lab personnel logged each sample into a bound laboratory notebook using a duplicate sample label. All observations and comments were noted in the notebook with black ink.

A traceability log was initiated for each sample as it was placed in its shipping container. The initial sample custodian of the samples from the MM5 train was the lab person who recovered the train. The log sheet (see Section 2.3.5.2) provided a historical record of who handled the samples. This log remained with the samples until the samples were transferred to the analytical lab custodian.

At the end of the test program, the shipping containers were packed in a single layer in the rear of the equipment truck. The containers were arranged so that the samples remained stationary and in an upright position throughout the transport. During transport, the appropriate samples were kept at 4° to 6°C (39° to 43°F), adding ice to the coolers when necessary.

2.1.6 Analysis

All MM5 samples were returned to the analytical lab for processing and analysis. When the containers arrived at the laboratory, the samples were transferred to the person who was to analyze the samples or prepare the samples for analysis. The transfer was documented on the traceability log sheets. The field sampling personnel handled the analysis for particulate and chloride at the analytical lab. All other analyses were conducted by the analytical personnel.

2.1.6.1 Particulate--

The samples from the front half of the MM5 train, consisting of the probe rinse, cyclone rinse (where applicable), front-half filter housing rinse, and the filter, were gravimetrically analyzed for total suspended particulates according to EPA Method 5 procedures. The filter blanks and

acetone blanks, at least two of each, were analyzed along with the samples using identical procedures. An acceptable blank value of acetone residue was less than or equal to 0.001% (≦ 0.001%) of the weight of acetone. Following the particulate analysis, the particulate catch in the acetone rinse residues and filters were given to the analytical lab. Subsequent metals analysis was performed on the filters (see Section 3.3.17).

2.1.6.2 Total Chloride--

The aqueous samples, KOH and condensate (60 mL aliquot), were analyzed for the concentration of total chloride. The analytical procedure followed is discussed in Section 2.4.3.2.

2.1.6.3 POHCs--

Particulate, XAD-resin, and condensate components of the train were extracted for semivolatile POHC analysis, using procedures discussed in Section 3.0 of this appendix. The two XAD-2 resin traps, the particulate filter plus the rinse residue, and the condensate were all analyzed for semivolatile POHCs. The concentrations found in the front-half and back-half of the train were reported separately. In addition, these same components were also analyzed for semivolatile PICs.

2.2 VOLATILE ORGANIC SAMPLING

2.2.1 Integrated Gas Sampling for Trace Levels of Volatile Organics Using a Tedlar Bag

The technique used to collect an integrated gas sample evolved throughout the test program. The following description outlines the sampling procedure in order to show the progression and variance from the proposed EPA method guidelines.

2.2.1.1 Scope and Application--

This method was used for the measurement of trace levels of volatile organics in stack gases. The procedure was designed to collect an integrated gas sample with a Tedlar bag. The procedure involved placing a Tedlar bag into a sealed box with the inlet to the bag connected to the sample line through a bulkhead fitting. The box was then slowly evacuated and the sample was drawn into the bag by the differential pressure. To minimize contamination of the bag sample prior to laboratory analysis, careful handling techniques, and strict leak check procedures were essential. Except for a few changes, the train and sampling procedure used follow the proposed EPA Method 23. The changes consist of adding a condenser and rotometer between the quartz probe and the sample bag and adsorbing the volatiles onto Tenax prior to GC/MS analysis.

2.2.1.2 Leak Check Procedures--

The gas bag sampling system was leak checked with a three-step procedure. The first check was for the bag itself, the second was for the bag and box assembly, and the final check included the entire train.

2.2.1.2.1 Gas bags--A pretest leak check was performed on each 15-L bag by pressurizing the bag to 0.5 to 1 kPa (2 to 4 in. of water) and allowing it to stand overnight. An inflated bag (Figure B-4) indicated no leakage. Prepurified nitrogen was used to inflate the bags, with the exception of the first test site where compressed air was used. The pretest leak check was conducted in the field laboratory at the first two test sites. The bags for subsequent test programs were checked at the lab prior to being sent to the test site and again at the test site prior to use. Clean Teflon line was used exclusively during the leak check procedure.

In the last four test sites an additional pretest bag leak check was performed. A dry test meter and rotameter were added to the system as shown in Figure B-5. The leak check was performed by evacuating the bag until 34 kPa (10 in. Hg) registered on the pump vacuum gauge. A consistent rotameter reading of 10 cc/min or less under these stringent vacuum conditions indicated the bag passed the leak check. The lid was then attached to the box.

2.2.1.2.2 Sample box--The sample box containing a labeled sample bag and a blank bag was leak checked prior to use on the stack. The equipment was assembled as shown in Figure B-6 and a vacuum was pulled on the box until a pressure differential of 2.5 kPa (10 in. H_2O) registered on the water manometer. The vacuum pump was then turned off and the manometer observed for 10 min. If any change in the manometer reading was observed the box was reassembled and rechecked until a stable vacuum was observed for 10 min.

In the last four tests the box was leak checked as shown in Figure B-7. To pass the leak check, a vacuum of 2.5 kPa (10 in. H_2O) was pulled on the box until a flow rate of 10 cc/min or less was observed on the rotameter.

2.2.1.2.3 Sampling train--The configuration of the sampling system initially used is shown in Figure B-8. The system was leak checked without the sample box and bag in-line. A rubber tube was used to connect the quick connects. The leak check was initiated by closing the valve in front of the impinger and the system evacuated to approximately 34 kPa (10 in. Hg). A flow rate of 10 cc/min or less on the rotameter was required to pass the leak check.

The leak check also involved checking the pump. The valve in front of the pump was closed, and a maximum vacuum was drawn. The tubing in back of the pump was clamped before turning off the pump. As the pressure on both sides of the pump equalized, the vacuum gauge was observed. The vacuum had to remain stable for over 1 min in order to qualify as leak-free.

Modifications to the sampling system (Figure B-9) were made before the last four tests to monitor more closely the flow rate into the bag. During the leak check of the system, a double-ended quick connect was placed in-line as shown in Figure B-10. The leak check was performed as described above with the exception of the adjustment of the rotameters and observation of the vacuum gauges. The sample line was evacuated until both vacuum gauges read approximately 34 kPa (10 in. Hg).

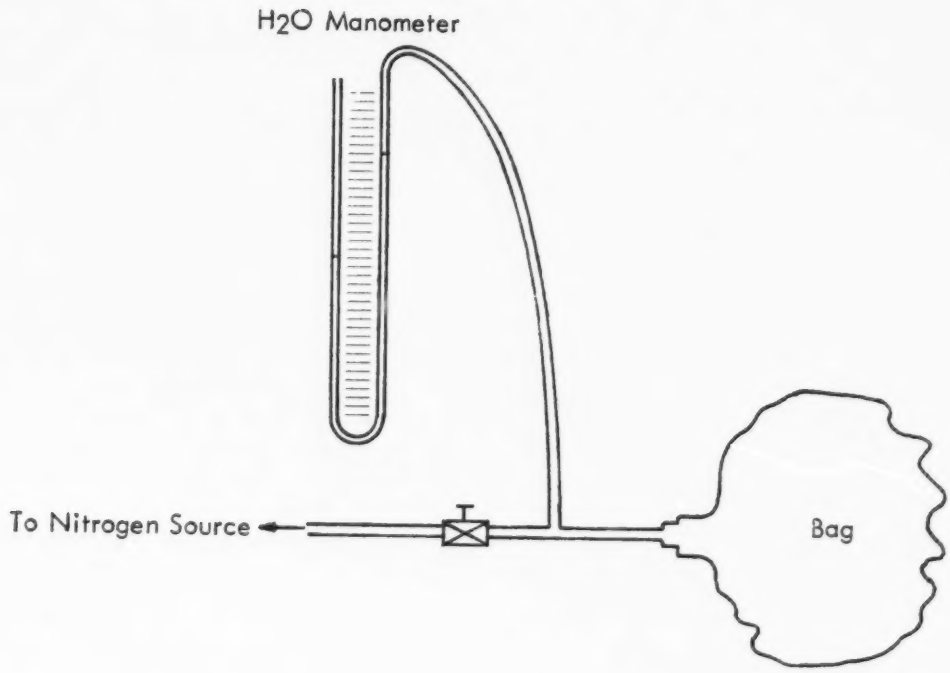


Figure B-4. Bag leak check system.

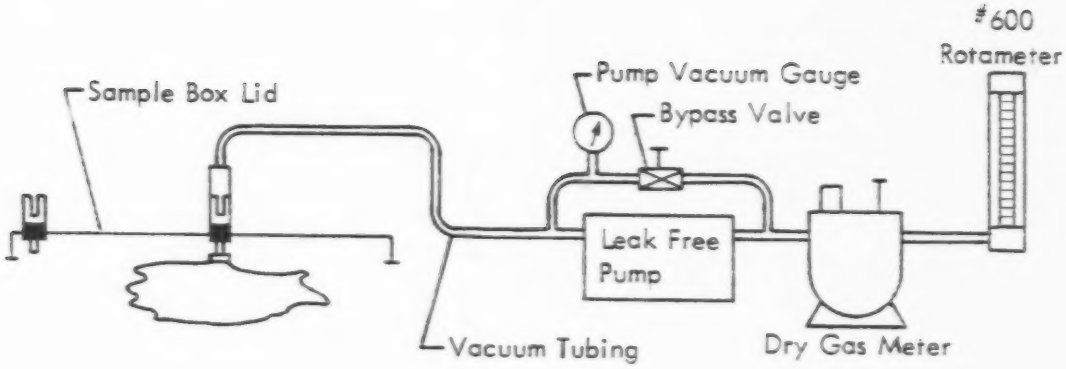


Figure B-5. Bag connection leak check.

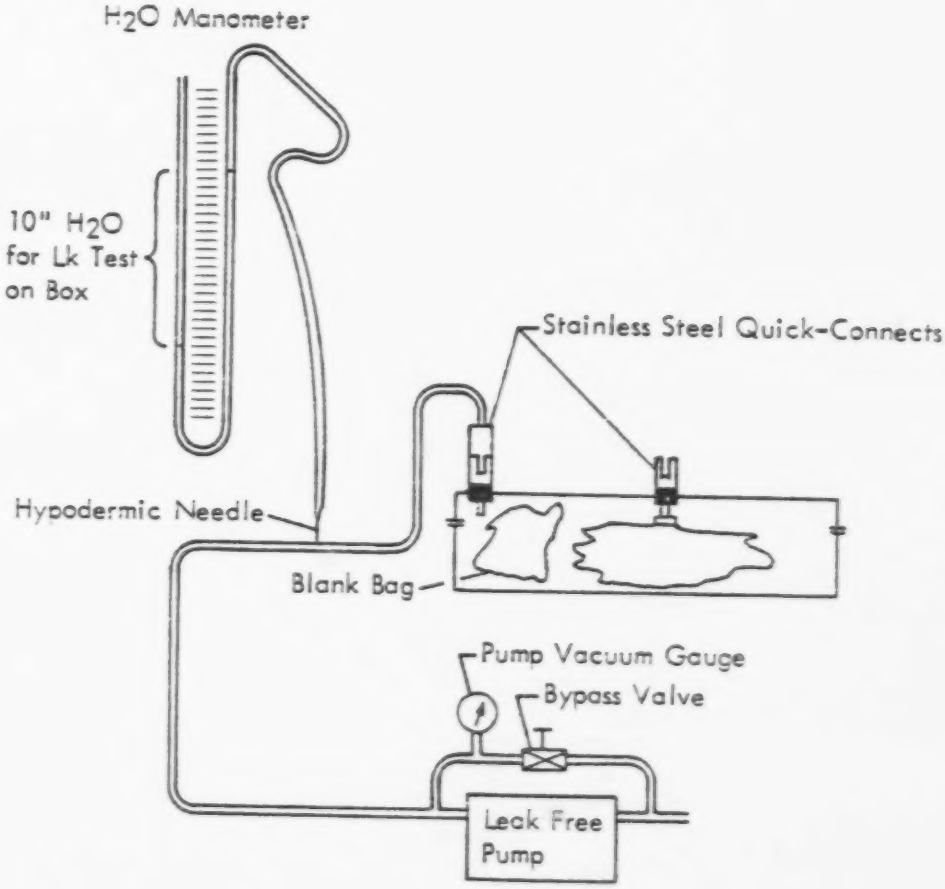


Figure B-6. Box leak check.

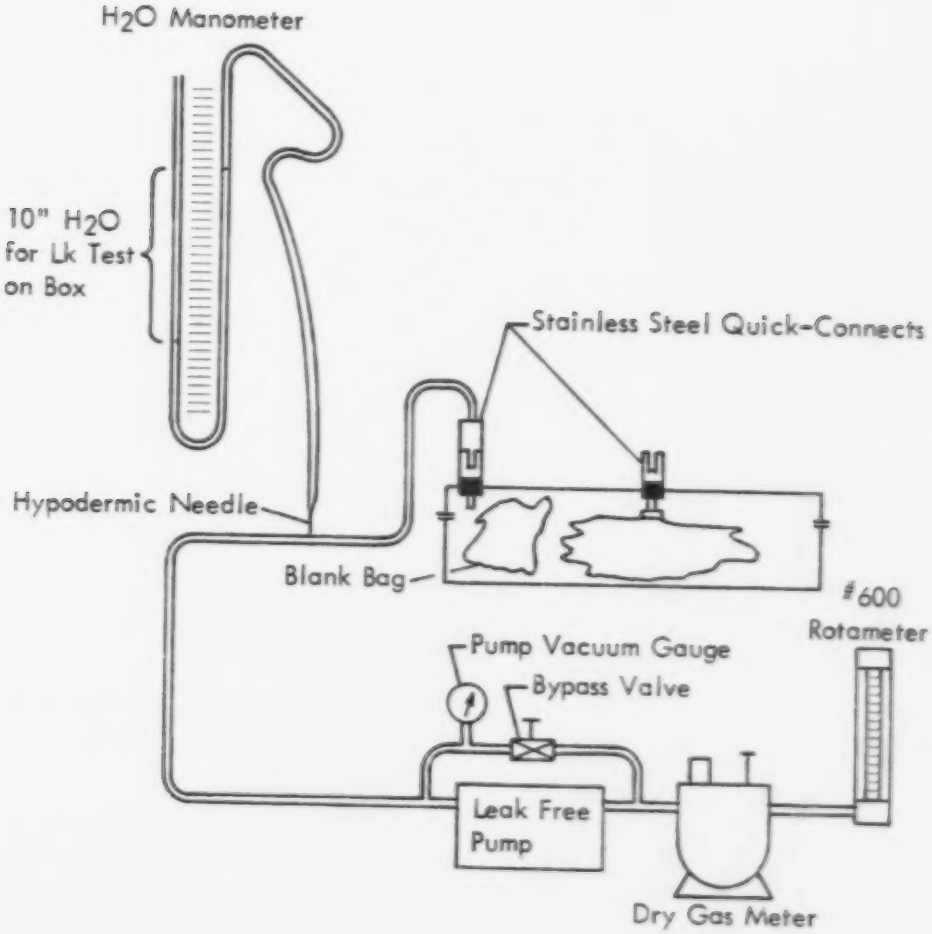


Figure B-7. Modified box leak check.

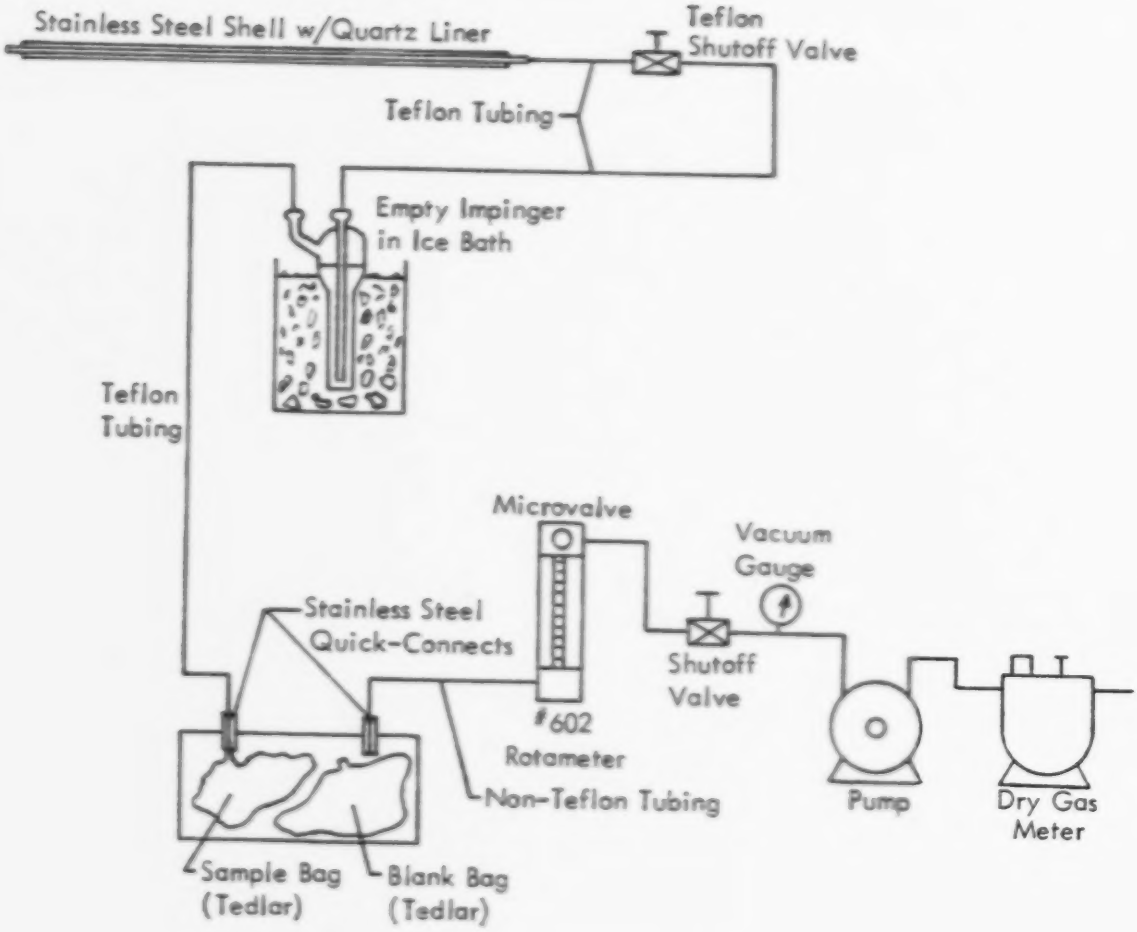


Figure B-8. Sampling system.

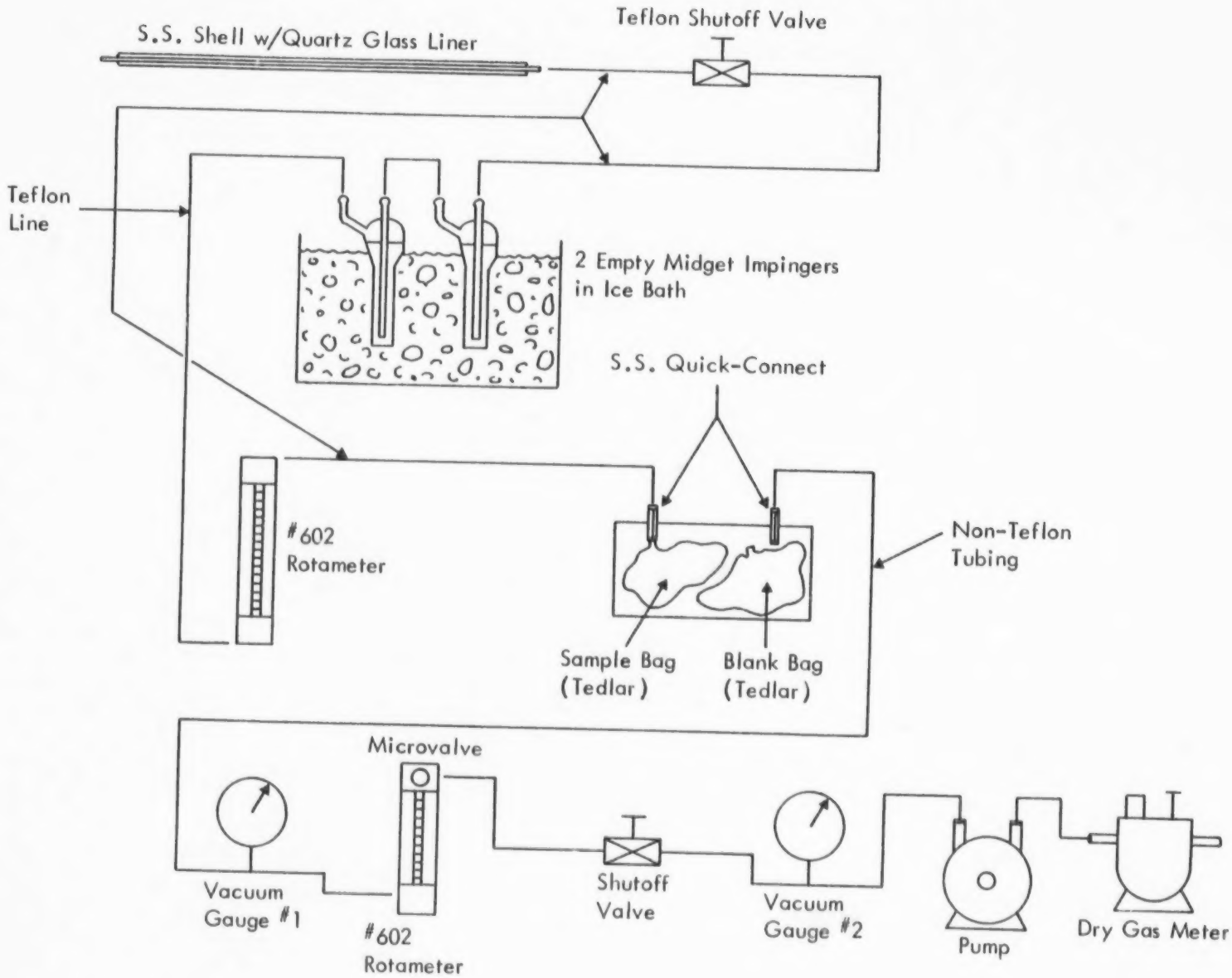


Figure B-9. Modified sampling system.

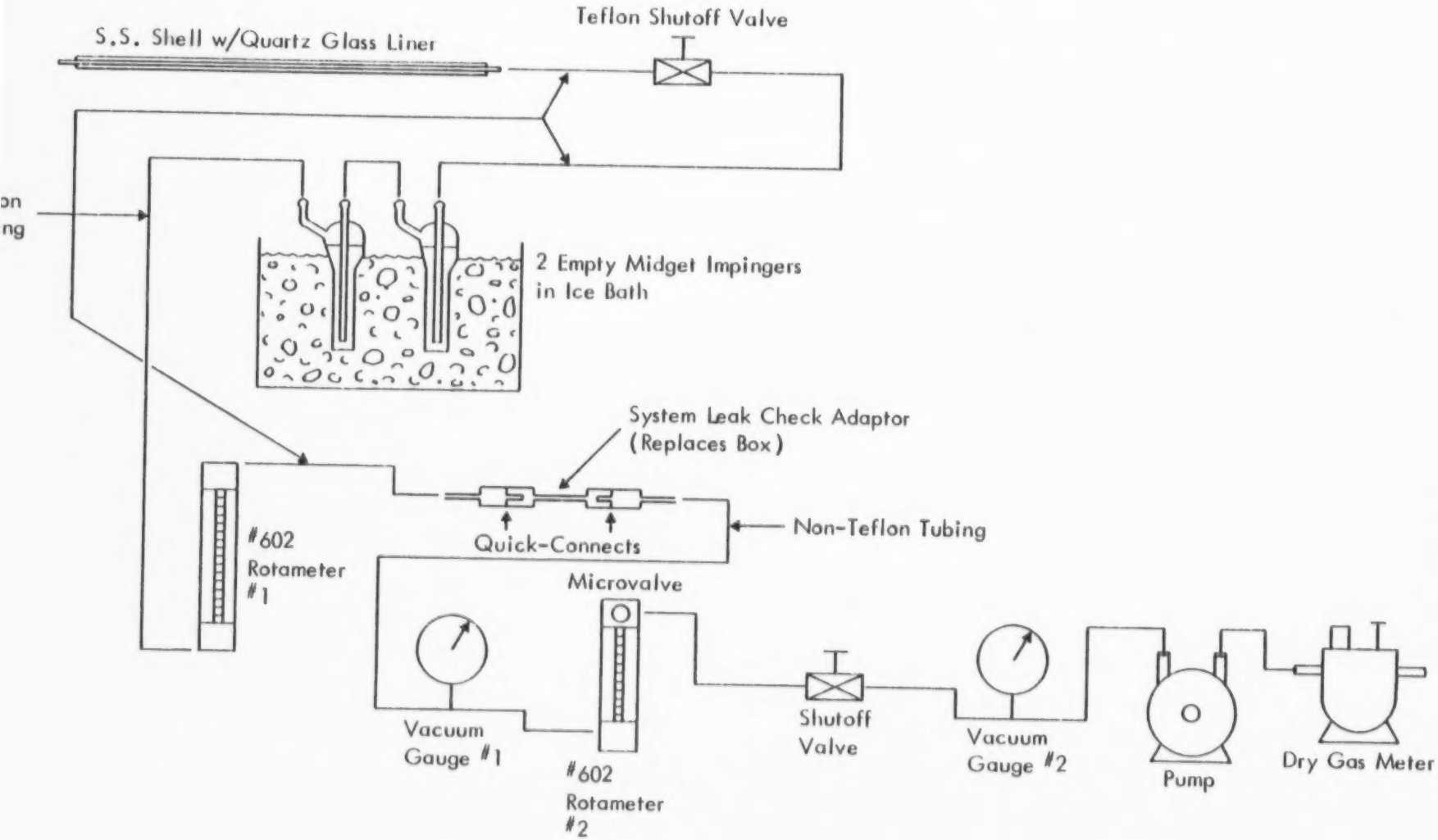


Figure B-10. System leak check without sample box.

When the valve in front of the pump was closed, vacuum gauge No. 1 was observed for leaks (see Figure B-10). The pump was checked as described above.

Prior to positioning the glass-lined sample probe in the stack, a visual check of the probe and the seal between the probe sheath and glass (or quartz) tube were conducted. The probe had been leak checked in the lab before being shipped to the field. If damage was suspected or observed upon field inspection, the probe was removed to the field lab for repairs and rechecking.

2.2.1.3 Sampling--

Sampling was conducted through ports located in the middle third of the stack. The probe was placed in the port and positioned ~ 1 m into the stack.

The sampling system was connected to the probe prior to connecting the sample box in-line with the system. With the valves opened and pump turned on, the system was purged for several minutes. The rotameter was set to the desired flow rate in order to pull approximately 8 L during a designated time period. Immediately before sampling, the pump was turned off and the sample box with the gas bag was connected in-line (Figure B-9). Sampling was inititated by turning on the pump and adjusting the rotameter, if necessary, to the proper flow rate. Readings were taken every 5 min and recorded on the data sheet. When the bag was half-full or at the end of the designated time period, the sample box with the gas bag sample was returned to the field laboratory for sample recovery. No samples were recovered from water condensed before the bag.

2.2.1.4 Sample Recovery and Shipment--

Immediately following sample collection, the gas bag was returned to the field lab for recovery. The bag was removed quickly from the sampling box and the inlet was plugged with a clean Teflon plug.

With the exception of the bags for the first test site, all gas bags were shipped to the field deflated and in a clean metal can in the equipment truck. Cardboard containers were used initially. After the second test site, activated charcoal packets were added to the cans to absorb any contaminants. The cans with the gas bags were then transported to and from the last four test sites in the cab of the equipment truck or were air-freighted to the analytical lab for analysis.

At Plant B and Upjohn 5-L of the gas from the bag was drawn through a Tenax cartridge as shown in Figure B-11. The bag was recapped and stored as described above. The capped Tenax trap was stored and shipped on ice.

A log of all samples was kept in the field in a bound laboratory notebook. In addition, a traceability log as described in Section 2.3.6, was initiated for each sample as it was placed in its shipping container.

2.2.1.5 Field Quality Assurance--

A field blank sample was taken each test day. A Tedlar gas bag was filled with prepurified nitrogen (N_2) in the field laboratory and then placed in either the same sampling box as the sample bag (Figure B-10) or

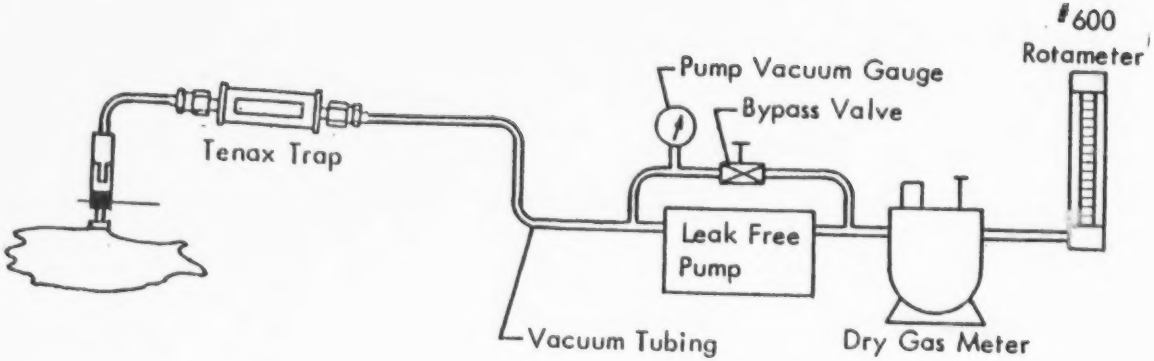


Figure B-11. Bag transfer to Tenax trap.

in a separate sampling box. The inlet to the bag was plugged securely. The box with the blank was transported up on the stack during testing. Following the completion of the test, the field blank was returned to the field lab to be recovered, logged in, and shipped in the same way as the actual gas bag samples.

2.2.2 Volatile Organic Sampling Train

The technique used to collect samples on Tenax and Tenax/charcoal tubes is described in this section. The sampling apparatus and procedures remained unchanged during the eight tests. The preparation of the sampling tubes and their storage did, however, undergo a number of changes during the first three tests.

2.2.2.1 Scope and Application--

This method applied to the measurement of trace levels (ng/L levels) of volatile organics in stack gases. The procedure was designed to collect gases on a Tenax absorbent contained in a glass tube. The initial Tenax trap was backed up by a second trap containing both Tenax and activated charcoal. A major effort was expended to assure that the traps are clean and leak free before sampling. Care was exercised to protect the traps from contamination during subsequent shipment to the field.

2.2.2.2 Equipment and Sampling Description--

The sampling train used on this project is shown in Figure B-12. The traps used to collect the samples are shown installed in the train in Figure B-12. Samples were drawn into the train through a glass or Teflon probe which contained a glass or quartz wool plug to remove particulate. The stopcock (S_1) was used to isolate the train from the stack during trap changes. The gas sample first passed through a condenser through which ice water was circulated. Condensate and gas then both passed through the first Tenax trap and into a collection flask where the liquid was removed. The gases then passed through a second ice water condenser and a second trap containing Tenax and charcoal. The gases then passed through a silica gel trap to remove water (for protection of the pump and rotameter), into a rotameter which was used to monitor and adjust flow to the desired rate. Finally, the gases exited through the pump into a dry gas meter where the sample volume was measured. The vacuum gauges shown on Figure B-12 were used for leak checking.

All lines in contact with the sample prior to the absorbant cartridges were either glass or Teflon. The fittings (C_1 through C_4) were stainless steel Cajon fittings with Viton O-rings. Ground glass joints were coated with Apeizon-L prior to testing to prevent leaks.

The design of the sorbent modules remained the same for all tests except that following the third test, the ends of the tubes were fire polished to prevent chipping and reduce leaks. The inner tube contains the absorbent. The outer tube serves only to protect the inner tube. Both tubes are sealed against the end plates with Viton O-rings. The Cajon fittings on the ends are different sizes to prevent placement of the tubes in the train backwards.

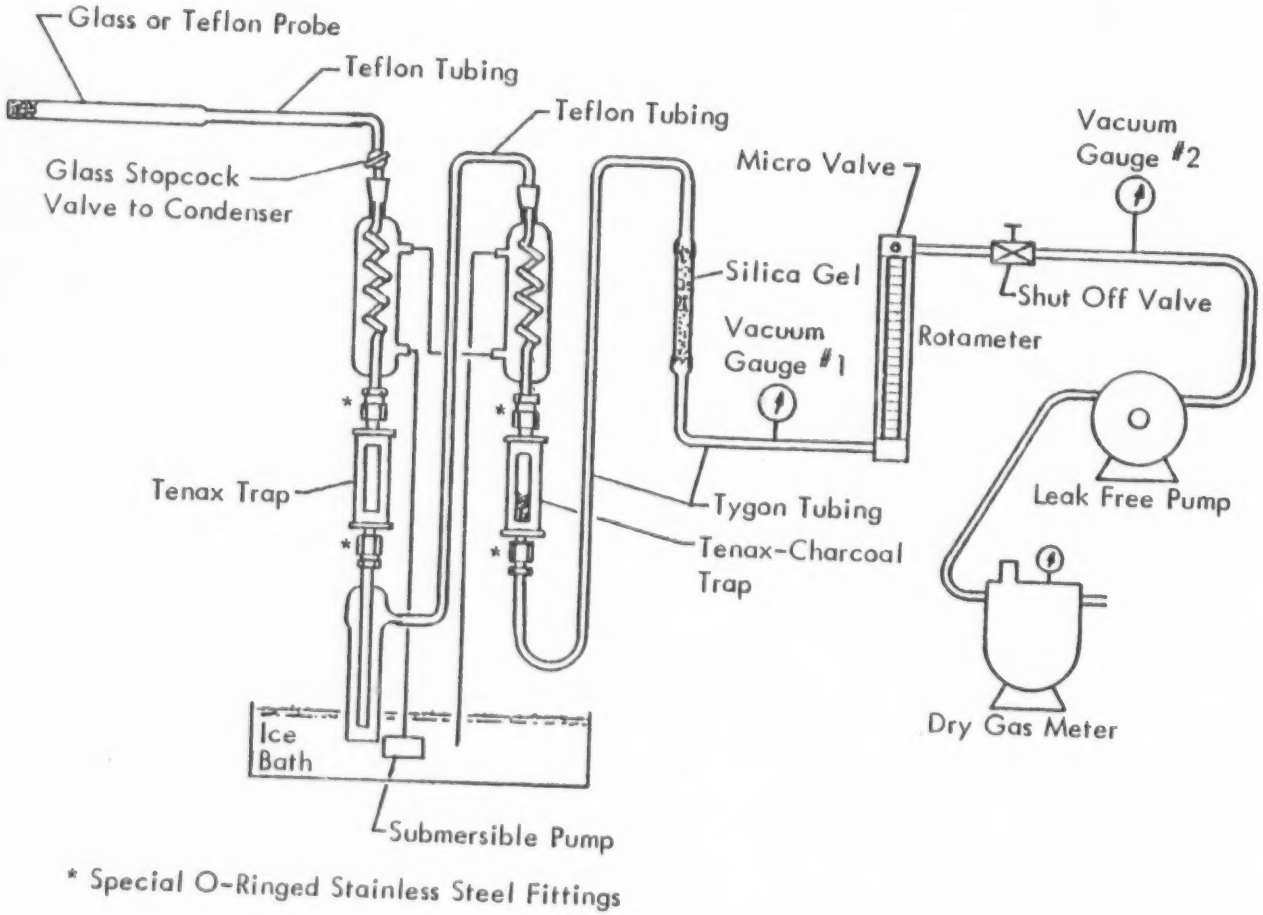


Figure B-12. VOS train.

2.2.2.3 Tenax and Tenax/Charcoal Cleanup and Trap Preparation--
The Tenax (35/60 mesh) and SKC petroleum-based charcoal (Lot No. 104) was initialy prepared by Soxhlet extraction for 24 hr with methanol. The sorbents were then dried in a vacuum oven at room temperature and packed into 10 x 1.6 cm glass traps with a minimum quantity of pre-extracted glass wool in each end to support the sorbents in the trap and between the Tenax and charcoal in the mixed traps. Later, stainless steel screens supported by stainless steel C-clips were used to support the Tenax beginning with the Mitchell test. The all-Tenax traps contain about 1.5 g of Tenax and the Tenax/charcoal traps contain about 1-g Tenax and 1 g of charcoal (two-thirds Tenax by volume).

The traps were thermally conditioned prior to use using the Nutech Model 322 thermal conditioning unit. The conditioning gas (nitrogen or helium) was purified by passing through a U-trap containing 5-angstrom molecular sieve immersed in liquid nitrogen. The temperature of the conditioning unit was adjusted to 240° to 260°C and the flow rate of gas through each trap was set to about 30 mL/min. The traps were generally conditioned for at least 4 hr each on two different occasions before being loaded into holders.

Following conditioning, each trap, which was engraved with a unique number, was transferred to a clean 25 x 150 mm screw-cap test tube also engraved with the same unique number. Prior to sampling, the traps were loaded into carriers for use in the field in the VOST. The traps were stored under ice water until used for collection of samples to retard the migration of Tenax degradation products, such as benzene and toluene, from within, to the surface of the resin. The traps were stored at wet-ice temperatures following sampling, until they were analyzed.

During the first few field tests with the VOST, the Tenax and Tenax/charcoal traps sometimes were observed to be severely contaminated with volatile organic compounds. Several possible sources of contamination were identified such as ambient air, contaminated metal carriers, O-rings, and the adsorbents. In order to prevent contamination, a series of stringent trap preparation procedures were tested and adopted which have proved very effective in eliminating the contamination for field sampling with the VOST. These procedures are discussed below.

2.2.2.3.1 Preparation of Tenax and charcoal--New Tenax and charcoal were Soxhlet-extracted with methanol for 16 hr, and dried in a vacuum oven at 50°C prior to packing into tubes. The Tenax and charcoal in packed tubes were not routinely re-extracted following sampling and analysis unless very high concentrations (i.e., micrograms) of sample components were collected.

2.2.2.3.2 Preparation of O-rings--The Viton O-rings were thermally conditioned in a vacuum oven at 200°C for 48 hr prior to use. This procedure removed volatile solvents which may be present in the O-rings and could outgas later.

2.2.2.3.3 Preparation of metal parts--The metal parts (including the stainless steel carriers, end plugs, C-clips, and screens) were sonified in

a warm-nonionic soap solution, rinsed with distilled water, air-dried, and heated in a muffle furnace at 400°C for 2 hr.

2.2.2.3.4 Preparation of glass tubes--The glass tubes were cut from new glass tubing, fire-polished, and annealed.

2.2.2.3.5 Packing--The Tenax and charcoal were packed into the glass tubes in an organic-free laboratory (laboratory air filtered through charcoal).

2.2.2.3.6 Trap conditioning--The traps were conditioned as described above. Two different conditioning periods were used of at least 4 hr each.

2.2.2.3.7 Trap assembly--The conditioned traps were assembled into the metal field carriers in the same organic-free room where the adsorbents were packed into the glass tubes.

2.2.2.3.8 Leak checking--The assembled field traps were checked for leaks by removing one of the end caps and attaching the trap to a source of organic-free nitrogen gas at 30 psi (2.1 kg/cm^2). The trap was then immersed in distilled water to check for the appearance of bubbles.

2.2.2.3.9 Trap monitoring--Following trap assembly and assurance that the traps did not leak, each trap assembly was attached to a manifold (capacity of 10 traps). Organic-free nitrogen was passed through each trap at a flow rate of 30 mL/min while the traps were heated to 190°C. The flow through each trap was sequentially monitored with an FID to check for emission of volatile organics from the trap assembly. Most traps showed no organic emissions, while others needed to remain on the conditioner for several hours until the emissions from the trap were reduced to less than a detectable level (< 2 ppb).

2.2.2.3.10 Trap storage--When the traps were shown to be clean with the FID, they were capped and stored under ice water until they were used for sampling. The traps were also placed back under ice water after sampling until they were analyzed by GC/MS. The ice water served to keep the traps cold which slows aging of the Tenax; i.e., the gradual transfer of compounds such as benzene and toluene from within the polymeric Tenax matrix to the surface of the Tenax where these compounds can be thermally desorbed during analysis and contribute to high background levels. The water also protects the traps from volatile organic compounds in the ambient atmosphere which could collect on the outside of the trap assembly and contaminate the adsorbents during disassembly just prior to analysis. A summary of the trap preparation procedures is shown in Figure B-13.

2.2.2.4 Sampling Procedure--

At each test site a new Teflon line was used to connect the VOST to the sample probe. The sample train was located as close as possible to the sample port. After leak checking, samples were collected at 1 L/min for 20 min. The sample flow rate was adjusted with the rotameter, and the sample volume was obtained from the dry gas meter. Six pairs of sample traps were sequentially placed in the sampling train during each run, for a total of 120 min of sampling time.

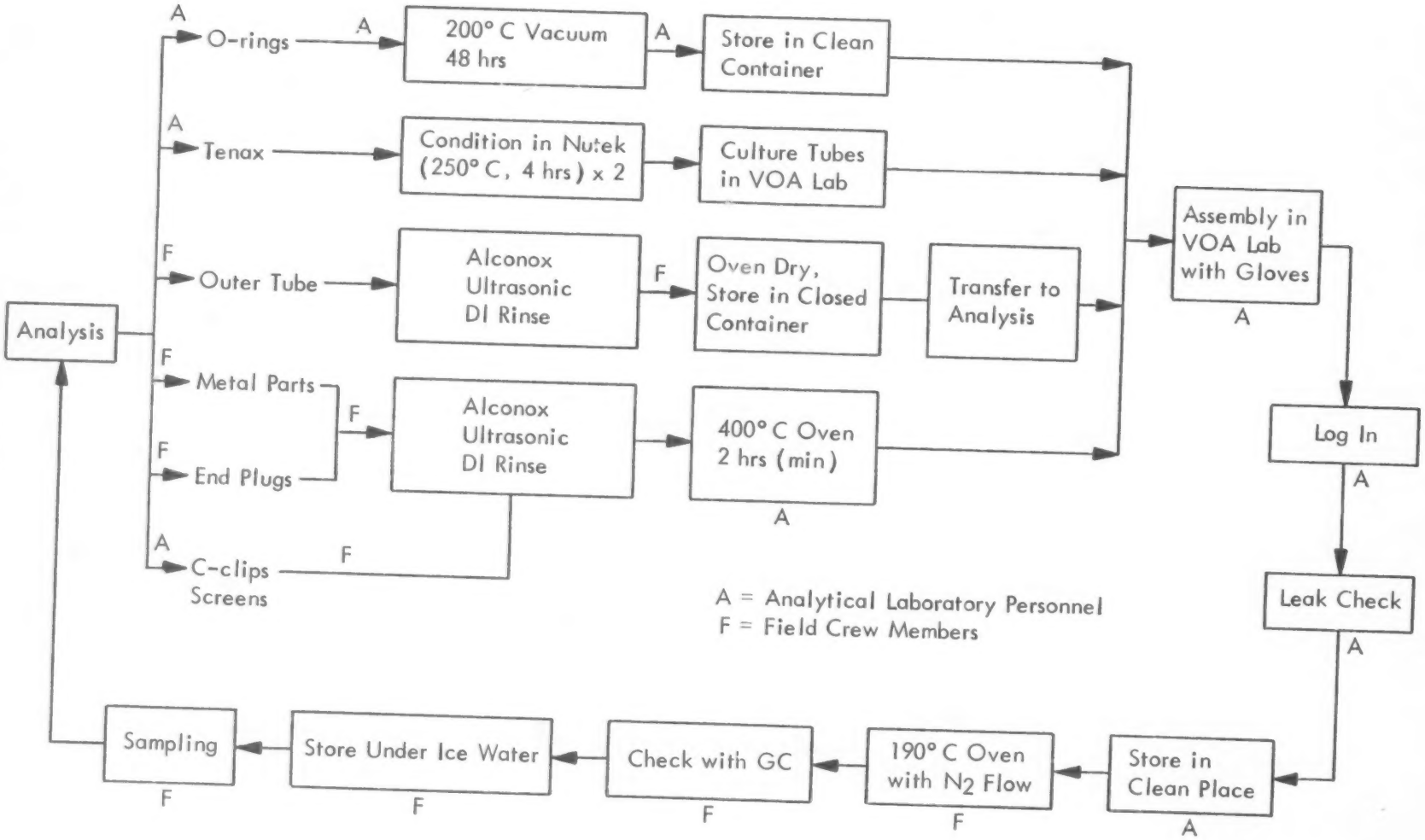


Figure B-13. VOST trap clean-up procedure.

Traps were transported to the stack under ice water in small coolers. The traps were removed just prior to sampling, placed into the train for sampling, and returned to the ice water immediately following the sampling.

2.3 GRAB SAMPLING

Grab sampling techniques were used when samples had to be obtained for a specific time period from sources or emissions which vary considerably in composition. A representative sample was obtained by preparing a composite from a number of subsamples or by taking multiple grabs at set time intervals.

Grab sampling methods were the best available means of sampling the waste feed streams, (drum waste, liquid waste, and fuel oil), ash discharge, and water streams (scrubber influents and effluents, where applicable). Some grab sampling of gaseous streams was also conducted.

In general, all containers for the grab samples were glass and were capped tightly with Teflon-lined caps at all times, except when adding a subsample. Appropriate labels were affixed to the sample containers after collection. Preservation and packing of the samples was unique for each type of sample. After proper packing, the samples were shipped to the analytical lab for analysis.

The subsections below discuss specific grab sampling procedures and on-site analysis procedures, as appropriate, for those grab samples. Individual subsections deal with procedures for waste feed streams, ash, water streams, and gaseous streams.

2.3.1 Waste Feed Streams

The waste feed streams and fuel oil were sampled to determine the input or mass feed rate of the designated POHCs into the process and other waste feed characteristics. Typically, the three types of feed streams were: liquid waste; solid waste; and fuel oil. Each type required a different sampling procedure in order to collect a representative sample. The waste types were fed into the incinerator in a variety of ways and have been characterized here as drum waste, liquid waste, and fuel oil.

2.3.1.1 Drum Waste--

Three of the test sites, Ross, Du Pont, and TWI received or prepared hazardous waste that was packaged in drums or similar containers. The drums contained solids, organic liquids, and highly viscous materials. Prior to testing, the drum wastes were staged, numbered, weighed, and sampled.

The appropriate drums were organized to obtain the desired waste composition and calculated feed rate as outlined in each test plan. Enough drums were staged to permit a 2 to 3 hr burn. The containers were organized in batches and labeled according to the order in which they would be burned. Each batch was weighed and the weights were used to determine the actual solids feed rate during each test. A grab sample of about 1 kg was collected from each drum or container fed into the incinerator. The samples

were composited to form a single sample considered representative of each type of solid feed for that respective test period.

2.3.1.1.1 Solids--Solid drum waste materials can be sampled using a trier, a trowel, an auger, and/or a grain thief. At the discretion of the sampler, the method was chosen for the solid waste in an attempt to collect the most representative sample. The subsections below describe the trier which was used at several sites, and the grain thief which was used at one site.

Sampling with a trier--(as described in EPA/OSW "Test Methods for Evaluating Solid Waste - Physical/Chemical Methods," SW-846).[2] A trier, a stainless steel sample corer, was inserted into the waste at an angle of 0 to 45 degrees and rotated 360 degrees to cut a core. With the trier's open side up, the sample was removed from the drum. With the aid of a wooden spatula, the sample was leveled in the trier and then transferred to a labeled glass container. The trier was scraped of excess waste and cleaned with acetone before use on another type of waste.

Highly viscous materials also were sampled with a trier. The trier was inserted into the material, rotated, and then pulled from the drum. The outside of the trier was cleaned before the contents were leveled and transferred to a labeled sample container.

Sampling with a grain thief--The grain thief, a hollow brass tube with a slotted outside sleeve, was inserted fully into the waste with the slots closed and the pointed-end first. To collect a sample, the sleeve was rotated to open the slots and the thief was shaken to permit entry of material. The slots were closed before removing the thief from the drum. The tube's contents were transferred to a glass sample container by inverting the thief and opening the slots. Care was taken in transferring the entire sample to the container. The grain thief was emptied completely before sampling other waste.

2.3.1.1.2 Drummed liquid organic--Most of the liquid waste drum samples also contained quantities of solids in the bottom of the drums. Samples were collected with the Composite Liquid Waste Sampler (Coliwasa) or with a 1-cm (3/8-in.) stainless steel tube fitted with an inlet valve. The Coliwasa (as described in SW-846) is a stainless steel tube (≅ 2.5-cm I.D.) fitted with a rubber stopper at the inlet attached to a center rod. With the inlet to the sampler fully open, the Coliwasa or stainless steel tube was slowly lowered into the liquid waste until the end reached the bottom of the waste container (if possible). To sample, the inlet was closed by lifting the center rod of the Coliwasa or by moving the lever to close the valve on the 1-cm (3/8-in.) tube. The tube was withdrawn quickly from the drum. It was necessary to allow the outside of the tube to drain momentarily. The tube's contents were emptied into a labeled glass container with the assistance of a funnel to prevent spills. The entire contents of each sampling operation were transferred fully to the sample bottle. The sampling devices were wiped and cleaned thoroughly with acetone before sampling other wastes.

2.3.1.2 Liquid Wastes--

Liquid waste samples, aqueous and organic, were drawn from a tap located in the respective waste feed lines at given time intervals over the test period. The volume and time of each aliquot collection was predetermined according to the test plan. Typically, 50 mL were collected every 15 min throughout the test period. This procedure resulted in a composite sample considered most representative of what was burned during the stack emission sampling test.

Before sampling from a tap, a sample line was attached to the tap outlet when possible. The tap was opened momentarily to flush the line and the waste material was properly discarded. If the sample line could not fit into the sample container or if there was no sample line, the use of a clean glass funnel or beaker was necessary. The funnel or beaker was rinsed with waste material before the collection of each sample.

For each aliquot, the tap was opened very slowly and the flow was adjusted to allow collection of the desired volume in less than 5 min. The clean glass sample bottle was marked externally to indicate equal portions based upon the number of aliquots required to fill the container in the allotted time frame of the test (~ 12 aliquots in 3 hr). The time of collection for each aliquot was recorded on the data sheet. The sample bottle was capped tightly except when adding an aliquot.

The tap was secured after collecting the final aliquot of the composite sample. Where applicable, the sample line was removed and discarded. The sample bottle was capped tightly and its contents were mixed thoroughly. Two subsamples from the composite were placed in 40 mL Volatile Organic Analysis (VOA) vials. The vials were completely filled so that no air bubbles were present when the Teflon septum caps were attached.

At TWI two types of organic liquid waste feed samples were taken during each test run. One type was collected and composited using the procedure outlined above. The other sample was taken correspondent to the grab samples of the stack gas using a gas bulb (see Section 2.3.4.1). The sample was taken using the procedure described above and placed in the 40 mL VOA vial. Analysis of the sample for carbon tetrachloride and trichloroethylene was performed on-site by a gas chromatograph with electron capture detection (GC/ECD) using the procedures described below.

The GC was a Varian 3700 with a Ni-63 EC detector. The separation column was stainless steel, 3 m x 3.2 mm, containing 20% SP-2100/0.1% Carbowax 1500 on 100/120 mesh Supelcoport (EPA Method 23, Halogenated organics).

The column was operated isothermally at 55°C (120°F). When heavyweight compounds were expected, the temperature was programmed up to 250°C (470°F) at 20°C/min after the completion of the isothermal run. Manual injection was used with a 10 µL syringe.

Each sample was injected at least twice. Due to unexpected attenuation changes, not all peaks were measurable. All peaks were compared against a

single mixed standard of 8 pg/μL CCl_4 and 7.3 pg/μL TCE (prepared by dilution from the 50:50 injector pump feed) in Burdick and Jackson n-hexane. All liquid injections were 1 μL. Peak areas were used for quantitation.

2.3.1.3 Fuel Oil--

Fuel oil was used at TWI as an auxiliary fuel during start-up and during nontest periods to minimize any possibility of contaminating subsequent test samples. The plant selected the desired operating temperatures and associated waste and fuel oil flow rates as well as excess air levels to achieve the desired operating parameters for a trial burn. The fuel oil was sampled to determine its contribution or input of POHCs into the process.

A single grab sample of fuel oil was taken for each test run. The sample was considered representative of the fuel oil burned during the stack emission sampling test. The oil sample was drawn from a tap located in the feed line or on the tank. A line was attached to the tap outlet. Before sampling, the tap was opened momentarily to flush the line and the oil was discarded properly. A clean glass sample bottle was used to collect the sample. The use of a clean glass funnel or beaker was often necessary in order to facilitate collection. The funnel or beaker was rinsed with the fuel oil before collecting the sample.

2.3.2 Ash Discharge

The ash discharge generated from the incineration of hazardous solid material was collected at six of the eight test sites. (Since the composition of the waste feed suggested that little ash would be generated at American Cyanamid and Upjohn, and collection of ash samples at these sites would have presented great difficulties, no ash samples were collected.) Where possible, the hopper or handling system for the ash was emptied prior to testing to ensure that the material sampled was representative of the residue of the waste burned during the test run. Grab sampling techniques were used to obtain samples of the ash. Due to the different designs of each of the incinerators and their ash handling systems, the sampling procedures and locations varied from plant to plant. The sampling procedure used at each test site and the sampling locations for ash collection are described below.

2.3.2.1 Ross--

Kiln ash was handled by an ash conveyor which discharged into a collection bin. A trier was used to remove kiln ash from the collection bin using the procedure outlined for drummed wastes in 2.3.1.1.1. These grab samples were collected to form a composite for each test run (~ 1 grab sample per hour). The ash was not a uniform material. Therefore, when the trier could not be rotated to cut a core, the sampler was used as a scoop to sample the material by inserting the trier at a 45 degree angle into the waste and lifting to remove the material. The sample was then transferred to a glass container with the appropriate label.

The main combustion chamber ash from the drum waste exited the chamber on skids by means of a conveyor (about one skid per hour). The trier was

used to remove a sample from each of the burnt-out barrels to form a composite of the ash on each skid. The material was allowed to cool before taking a sample. The same sampling procedure was followed as described above. At the end of the test run, the samples of ash from each skid were combined to form a single composite sample to represent the ash discharge during the entire test run. An appropriate label was affixed to the glass sample container.

2.3.2.2 Plant B--

While no ash sample was collected at Plant B, the particulate catch in the pollution control equipment was sampled. Three grab samples were collected to form a composite for each test run (~ 1 grab sample per hour). A trier was used to remove subsamples from the hopper using the same procedure outlined in 2.3.1.1.1. The glass sample container was sealed tightly and tagged with the appropriate label.

2.3.2.3 Zapata--

During normal operations, only liquid wastes were burned in this small incinerator. Very little ash was expected. However, wooden pallets were burned during start-up operations. At the end of the test program, a single grab sample of the ash was collected from the bottom of the incinerator. The procedure followed was identical to the one outlined in 2.3.1.1.1.

2.3.2.4 Mitchell--

The incinerator burned only liquid wastes. Due to its size, the facility did not have an ash handling system. The ash was collected at the bottom of the incinerator and removed manually when the system was not operating (about once a week).

At the end of the test program a single grab sample of the ash was collected by plant personnel and shipped to the analytical lab. Personnel were instructed to collect a sample as representative as possible of the waste residue. The procedure discussed in 2.3.1.1.1 was used as a guideline to instruct the samplers. A labeled sample bottle and appropriate shipping container was left with the plant.

2.3.2.5 Du Pont--

The kiln ash was continuously sluiced with water to a clarifier tank. The kiln ash samples were collected from a tap in the feed line to the clarifier. At this location, the material was an ash slurry composed mainly of water. Three grab samples were taken during a test run to form a composite sample (approximately one grab sample per hour). Using 2-L glass containers, samples were collected according to procedures described in 2.3.1.1.2. The containers were marked externally to indicate three equal portions which would fill the container.

2.3.2.6 TWI--

The ash was discharged by a manual ram located at the bottom of the chamber. The material then dropped from the chamber onto a drag chain where it was conveyed and deposited into a bin. The ash ram was operated on the average of five to six times per hour.

For collecting ash, a glass beaker or other glass container was attached to a metal rod. As the ash was emptied from the drag chain, the container was held underneath to catch a sample. Equal portions were collected in each grab and were taken whenever the ash was discharged (approximately five to six times per hour). All grab samples were composited to form a single sample for each test run. Transferring of the material from the collection container into a labeled sample bottle was facilitated by the use of a glass funnel and a spatula.

2.3.3 Water Streams

Quench sections and scrubber devices for pollution control were part of five of the incinerator systems tested: Ross, Plant B, Upjohn, Du Pont, and TWI. All of the water entering and leaving the incinerator systems at these plants was sampled.

Grab sampling techniques were used to collect a representative water sample from each available sampling location during a test run. In general, samples were collected of the make-up water supply (city water, well water, or lake water); influents to the quench and scrubber, including recirculated water; and effluents from the quench and scrubber. The frequency of sampling, the location of the sampling points, and the volume of each sample was predetermined according to the test plan for each incinerator.

The make-up water samples were drawn from taps located in the supply lines. A clean, glass 2-L bottle was used to collect the samples. The single-grab sampling procedure followed was identical to the procedure described in 2.3.1.3. Immediately after sampling the sample bottle contents were mixed thoroughly. Two subsamples from the composite were placed in 40 mL VOA vials. The vials were completely filled so that no air bubbles were present when the Teflon septum caps were attached. The composite sample bottle was recapped tightly. All samples were labeled appropriately and placed in proper shipping containers.

The quench and/or scrubber influent and effluents were sampled using the same methods as those used to sample the make-up water, except that three aliquots of equal volume were collected rather than one grab sample. VOA vials and sample handling procedures were identical.

At TWI the return water from the quench and separator emptied into an open tank in which the solids settled to the bottom. After the final test run, a grab sample of the solid material was collected with a glass beaker attached to a metal rod. The beaker was submerged into the tank until it hit the bottom. A sample of the solids was obtained by scooping or dragging the beaker across the material and then retrieving the container from the tank. Excess liquid was drained off before scraping the material from the beaker into a clean glass sample jar. A spatula and glass funnel were used to aid in the transfer. Approximately 10 g of sample were collected. The sample was labeled and placed in the proper shipping container.

2.3.4 Gaseous Streams

Grab sampling of gaseous waste feed was necessary at one site (Upjohn). The incineration facility at Upjohn burned a combination of gaseous waste and liquid waste. The gaseous waste consisted of vent gases from production units. Three gaseous constituents in the vent gas were sampled and analyzed in order to characterize the waste feed.

At TWI, grab samples of the stack gas effluent were taken in conjunction with organic liquid feed samples in order to analyze the material on-site for specific POHCs.

Evacuated glass containers were the recommended apparatus used for gas collection. The three types of containers used included 250 mL glass gas bulbs with stopcocks at each end, 5 and 10 mL gas-tight syringes, and 2-L round bottom flasks with T-bore stopcocks at the opening. After sampling, the gaseous constituents either were absorbed by chemical reagents in the container or retained in the gaseous phase for later analysis.

2.3.4.1 Collection of Gas Grab Samples in a Glass Bulb--

The following sections describe the equipment sampling procedures and on-site analytical procedures when gas grab samples were collected in glass bulbs.

2.3.4.1.1 Equipment--The following equipment was used for sampling:

- Probe of borosilicate, quartz glass tubing, or Teflon.
- Teflon tubing (1/2-in. OD); sufficient length required to extend from the center of the stack, or end of the probe, to the sampling bulb.
- Tight fitting port seal around the probe.
- Glass on Teflon shut-off valve.
- Glass gas bulbs or collection vessels, 250 mL volume, with stopcocks on both ends.
- Leak-free pump.
- Dry gas meter.

Only glass or Teflon was used from the probe tip to the glass sample tube. All glassware, probes, and lines were cleaned with soap and rinsed repeatedly with deionized water followed by a final rinse in spectra grade methanol. The equipment was then oven dried at 150°C (300°F). Stopcocks were greased with Apiezon L.

2.3.4.1.2 Sampling procedure--The sampling procedure and train assembly was modified slightly to fit each test situation in order to obtain a representative sample. In general, the probe was inserted in the port, and the

area around the probe was sealed securely to prevent dilution of the sample. A gas bulb was purged with a 2-1/2 L gas sample prior to isolating a sample. Gas bulb grab samples were taken at two of the test sites.

2.3.4.1.2.1 TWI--Grab samples of the stack effluent were taken from a port 3 m (10 ft) above the base of the stack. The sampling train was assembled as shown in Figure B-14. A moisture trap was placed in line prior to the gas bulb to collect condensate. With both bulb stopcocks open, the probe valve was opened, and the pump was switched on to purge the system. A volume of 2-1/2 L of gas was used for purging. A sample was isolated by closing both stopcocks on the bulb. The probe valve was closed, and the pump was shut off before removing the glass bulb from the system. The sample container was labeled and returned to the field lab for on-site analysis. Three grab samples were collected during each test run. After the final test run, the three grab samples were placed in the appropriate shipping container and transported to the analytical lab for analysis.

2.3.4.1.2.2 Upjohn--The above procedure was modified slightly to sample a gas containing significant quantities of phosgene. A double ended squeeze bulb was used in place of a pump and dry gas meter, as shown in Figure B-15. The bulb exhaust was directed into a bucket filled with caustic absorbant to destroy excess phosgene. To purge the system, the squeeze bulb was pumped 10 times. Both stopcocks were closed on the collection vessel to isolate a sample. Before removing the sample container from the system, the probe valve was closed, followed by squeezing the rubber bulb. The squeeze bulb was pumped several more times to clear the lines after the glass bulb was disconnected. Two grab samples were taken during each test run. Each sample container was labeled and placed in the appropriate shipping container.

2.3.4.1.3 Analysis on-site for carbon tetrachloride and trichloroethylene--At TWI a laboratory gas chromatograph equipped with an electron capture detector (GC/ECD) was operated at the field site as an experimental attempt to obtain more timely determination of DRE. This instrument was used for the analysis of both the 250 mL glass bulb samples of stack gas and the liquid waste feed samples.

The GC was a Varian 3700 with a Ni-63 EC detector. The separation column was stainless steel, 3 m x 3.2 mm, containing 20% SP-2100/0.1% Carbowax 1500 on 100/120 mesh Supelcoport (EPA Method 23, Halogenated organics).

The column was operated isothermally at 55°C (130°F). When heavyweight compounds were expected, the temperature was programmed up to 250°C (480°F) at 20°C/min (36°F/min) after the completion of the isothermal run. Manual injection was used with a 10 μL syringe for liquids and a 5 cc gas-tight syringe for gas samples.

Each sample was injected at least twice. Due to unexpected attenuation changes, not all peaks were measurable. All peaks were compared against a single mixed standard of 8 pg/μL CCl_4 and 7.3 pg/μL TCE (prepared by dilution from the 50:50 injector pump feed) in Burdick and Jackson n-hexane.

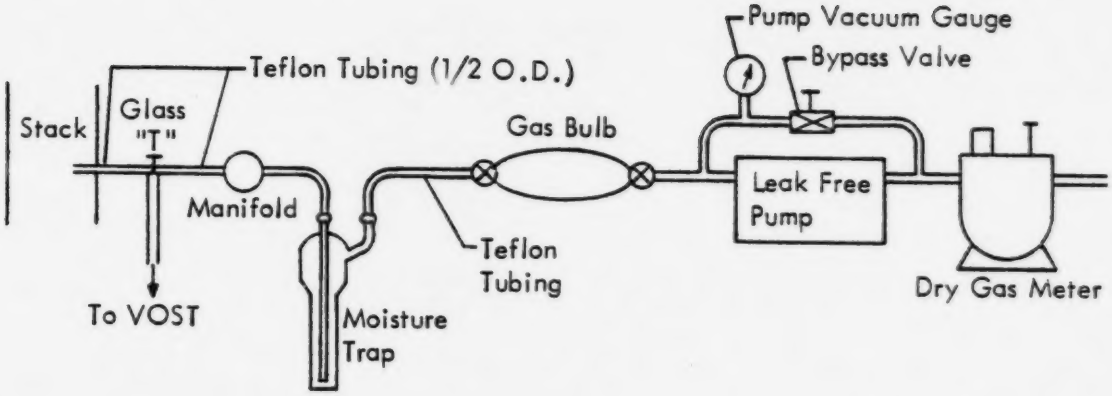


Figure B-14. Glass gas bulb sampling system.

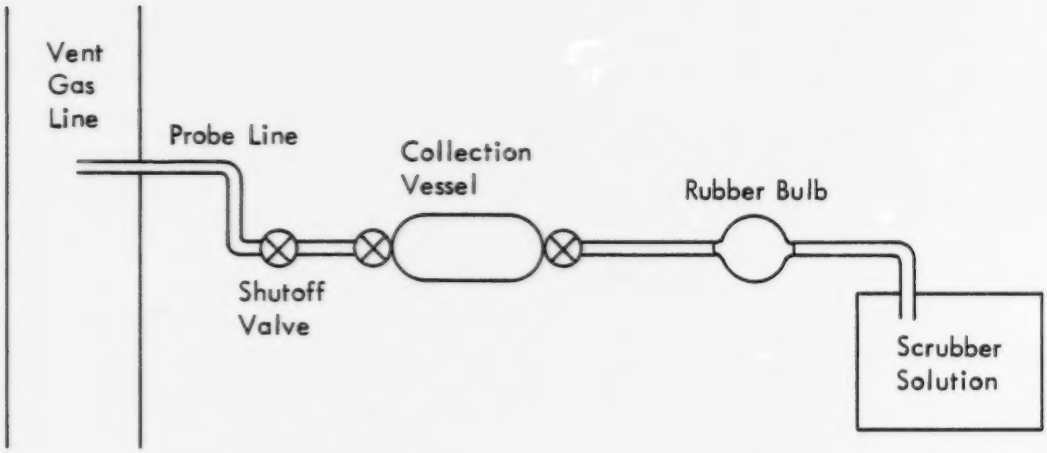


Figure B-15. Glass gas bulb sampling system; modified for sampling concentrated chlorinated gases.

All liquid injections were 1 μL and all gaseous injections were 1 cc. Peak areas were used for quantitation. The difficulty in preparing a clean gas standard and compensating for the syringe blank made a separate gas standard impractical.

During run Nos. 1 and 2, the gaseous samples were found to have a high blank value associated with the syringe or the special long needle required to reach past the bulb stopcock. The blank decreased with repeated use and depended upon how the syringe was filled with cylinder nitrogen. The syringes were baked out and flushed with hexane with some success, but a greater improvement was noted after the raw liquid waste feed samples were removed from the room at the start of run No. 3. With only diluted liquid samples present in the area, the blanks gradually decreased and remained low. Blank values with the liquid syringe were always undetectable.

Once the bulbs had come to room temperature, the long needled gas syringe was put into the bulb through the septum, the stopcock was opened and the syringe pushed into the bulb to its limit (3 to 4 in.). The plunger was then pulled out to the 1 cc mark and was allowed to sit undisturbed for 5 min. The needle was then withdrawn after the stopcock on the syringe was closed. The needle was replaced with a smaller gauge needle and the syringe contents were injected onto the column.

2.3.4.2 Collection of Gas Grab Samples in a Syringe--

Collection of gas samples in a syringe was chosen as the best available method for the collection of noncondensing gases containing significant quantities of phosgene. Due to the high toxicity of the vent gas feed at Upjohn, stringent safety measures were applied when collecting and handling samples. A gas-tight syringe was a suitable collection container for safely and simply grabbing a gas sample. The sample was collected in the syringe and then injected into an absorbing reagent for analysis.

2.3.4.2.1 Equipment--The following equipment needed for sampling as shown in Figure B-16 was:

- Teflon tubing (1/4 in. OD); sufficient length required to extend from the center of the stack to the sampling container.
- Tight fitting port seal around probe.
- Glass or Teflon shutoff valve.
- Gas tight syringes, 5 and 10 mL volume with valve.
- Teflon tee-fitting with rubber septum mounted on one leg.
- Double-ended rubber squeeze bulb.
- Bucket filled with caustic absorbent to destroy excess stack gas.
- Heavy-walled rubber tubing.
- Hoffman clamp.

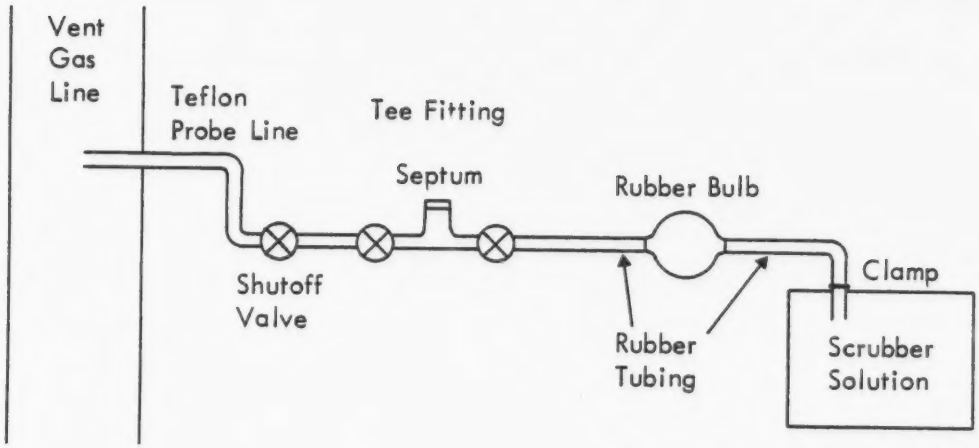


Figure B-16. Gas collection with a syringe.

Only glass or Teflon was used from the probe tip to the collection vessel. No stainless steel was used in the system. The syringe, stopcocks, shut-off valve, and probe lines were cleaned with soap and rinsed repeatedly with deionized water followed by a final rinse in spectra grade methanol. The equipment was then oven dried at 150°F (300°F).

2.3.4.2.2 Sampling procedure--The probe was inserted into the port and the area around the probe was sealed securely. The sampling system was assembled as shown in Figure B-16, keeping the port valve closed. Stopcocks were greased with Apiezon L. After opening the port valve, the sample line was purged three times by squeezing the bulb. With the syringe valve open, the syringe needle was inserted through the in-line septum. The syringe was filled completely, the gas was expelled back into the fitting, and the squeeze bulb was pumped once. This step was repeated three times to flush the syringe. Gas was then drawn in again to fill the syringe and expelled until a volume of 2 mL was remaining. Before withdrawing the needle from the septum, the syringe valve was closed and the probe valve was secured tightly. The sample was labeled and returned to the lab for on-site analysis. Two grab samples were taken during each test run.

2.3.4.2.3 Analysis on-site for phosgene--At the end of each test run at Upjohn, the gas samples in the syringes were analyzed on-site for phosgene. In addition, the samples of stack gas collected in the midget impinger train also were analyzed for phosgene. (Section 2.4.2 describes sampling for phosgene with the midget impinger train.) The analytical method used was the National Institute for Occupational Safety and Health (NIOSH) Manual for Analytical Methods, Volume 1, Method No.: P&CAM 219, "Phosgene in Air" (April 1977).

P&CAM 219 is a colorimetric analysis using nitrobenzyl pyridine in diethyl phthalate as both absorbing solution in the train and the color reagent. The absorbance is measured at 475 mm with a normal instrument range of 5 to 500 μg of phosgene.

Modifications in the analytical method were as follows: a liquid standard of phosgene (1 mg/mL) dissolved in diethyl phthalate was prepared at the analytical lab and taken to the field site for subsequent dilution for the working standard. A 1 or 2 mL volume from the gas-tight syringe was injected into a 40 mL Teflon faced septum vial containing 10 mL of the color reagent. The vial was shaken and the solution was analyzed with the spectrophotometer. Additional dilution with color reagent was used as necessary to keep the sample absorbance within the calibration range.

2.3.4.3 Collection of Gas Grab Samples in an Evacuated Flask--

A grab sample of gas was collected in an evacuated flask and absorbed in reagents for determination of total vaporous inorganic chlorides and chlorine. The sample was absorbed in sodium hydroxide, and the hypochlorite formed from chlorine was reduced to chloride by the addition of sodium arsenite. A modified EPA Method 7 was used to measure chlorine, hydrogen chloride, and phosgene.

2.3.4.3.1 Sampling procedure and recovery--The sampling apparatus, assembly of the train, and sampling procedures were identical to those described in EPA Method 7 guidelines. Sample recovery procedures and reagents were modified to absorb specifically chlorine and hydrogen chloride. A 10% sodium hydroxide solution was used as the absorbing solution. No absorbing solution was added to the flask prior to sampling. Other reagents included a 20% sodium arsenite solution, used as a reducing reagent, and double-distilled or deionized water. All chemicals were ACS analytical reagent grade.

Two grab samples of the vent gas were collected in evacuated flasks during each test run. Immediately following collection of a sample, the flask was removed to the field laboratory for recovery. A mercury filled U-tube manometer was connected to the flask, and the valve from the flask to the manometer was opened. The flask temperature, barometric pressure, and the difference between the mercury levels in the manometer were recorded on the data sheet.

After disconnecting the manometer, a 50-mL buret with an adapter was attached to the stopcock. Fifty milliliters of the 10% sodium hydroxide solution were added to the buret, and the buret stopcock was opened. The three-way stopcock on the flask was opened slowly to allow the absorbing solution to enter. The three-way stopcock was closed when 50 mL were added to the flask, and the buret was disconnected. The flask was then shaken for 1 min to insure complete reaction of the sodium hydroxide with the gas sample. The sample solution was transferred from the collection flask to a clean 100 mL polyethylene sample bottle.

The flask was rinsed three times with approximately 5-mL portions of distilled water. The rinsings were added to the sample bottle along with 5 mL of the 20% sodium arsenite solution. The bottle was capped tightly, and the contents were swirled to mix the solution. An appropriate label was affixed to the sample bottle.

2.3.4.3.2 Analysis for chlorine--After return to the laboratory, the samples were analyzed by a modified Volhard Titration method developed by the U.S. Department of Health, Education and Welfare.[3] After measurement of the total sample volume, an aliquot of each sample was taken in triplicate in 250 mL Erlenmeyer flasks. Silver nitrate (0.1 M) was added from a burette until it was in excess and the AgCl formed had coagulated. After coagulation, the AgCl was filtered off and indicator solution was added. The excess Ag^+ was then back titrated with thiocyanate until a stable reddish-brown end point was reached.

The total chlorine (Cl_2) content of each sample was calculated from the net amount of $AgNO_3$ consumed. The ppm of Cl_2 in the gas sample was then calculated from the known gas volume and the total Cl_2 determined by the modified Volhard Titration.

2.3.5 Sample Handling and Shipping

After collection, the samples were packaged and stored in the field laboratory to prevent sample loss and to maintain sample integrity. Since

the Department of Transportation regulations restrict shipment of certain hazardous materials in commercial carriers, the most expeditious means of transporting the samples to the analytical laboratory was to truck them. At the end of each test program, all grab samples were loaded carefully in the rear of the sampling equipment truck and transported to the lab.

2.3.5.1 Handling--

All nongaseous grab samples were collected in or transferred to airtight glass containers with Teflon-lined lids. Immediately after the collection or transferring of a sample, the container was labeled and capped tightly to prevent loss of material and volatiles. Tape was used to seal the container lid for extra protection. The height of the sample material or fluid level was marked on the exterior of the sample bottle to determine if leakage occurred before analysis.

All labels were preprinted by computer and provided in triplicate to the sampling crew prior to each test program. The format of each label included the plant name, run number, unique sample number, description of the contents, date, and sampler's name. The sample number was an encoded 11-digit number providing identification of the plant, test run, and sample type. This number was primarily used for sample tracking. Additional information was entered by hand in the field. Typically, the date, sampler's name, and subsampling designations were the only entries. Although the labels were self-adhesive, transparent tape was overlaid on the completed label as it was affixed to the sample container.

For preservation of the sample before analysis, the sample bottle was placed in a polyethylene bag and secured with a twist tie. The wrapped sample bottle was placed in a cooler which served as a refrigerated storage container as well as a shipping container. The coolers were kept at 4° to 6°C using ice in sealed bags. Each cooler contained only one type of sample (i.e., liquid waste; scrubber effluent).

The gaseous grab samples collected in glass gas bulbs were handled as little as possible and packed carefully for shipping. After collection, the vessel was labeled and both stopcocks were secured with tape in the "closed" position. At Upjohn, each bulb was packed in a metal can with enough vermiculite to prevent breakage. The cans were sealed and a duplicate sample label was affixed to the can. At TWI, each of the three gas bulb samples from the final test run were packed in a cardboard box with packing peanuts to prevent damage. The boxes were taped shut and assigned container numbers.

The paint waste feed at Du Pont was packaged in metal cans and placed in drums to be fed into the kiln. One grab sample was taken from every batch of waste paint drums, which consisted of one can of each different type or color of paint. Each sample was labeled and packed in a numbered cardboard box with sufficient packing material. The grab samples were packaged products in sealed cans, and therefore, not refrigerated.

2.3.5.2 Sample Log--

A log of all samples was kept in the field as the samples were generated. When the last grab sample was added to the composite, or when a sample was complete, it was returned to the field lab. The designated lab person made sure that the samples were labeled and packaged carefully for storage and shipping. In addition, the lab personnel logged each sample into a bound laboratory notebook using a duplicate sample label. All observations and comments were noted in the notebook with black ink.

A traceability log was initiated for each sample as it was placed in a cooler or shipping container. One log sheet was filled out in duplicate for each container or type of sample. The log sheet, shown in Figure B-17, included the date, the type of sample, the shipping container number, the sample number, and the name of the sampler. This sheet provided a historical record of who handled the samples.

The designated lab person served as the sample custodian for all samples in the field. The initial sample custodian was the person who collected the grab sample. At the end of the test run, sample custody was then transferred to the lab person. Each time sample custody was transferred, the samples were inventoried and recorded on the traceability log sheet in the appropriate columns. As the samples were inventoried, the contents level marked on the exterior of the sample bottle was confirmed. Any changes in the level or in the sample itself were noted and dated on the sheet.

At the end of the test program, the custody of all samples being trucked to the analytical lab was transferred to the driver of the truck. Samples never changed custody without being inventoried and signed off on the log sheet. The original traceability log sheet traveled with the samples until the samples were transferred to the laboratory custodian. The duplicate log sheet was kept by the field sample custodian.

Those samples which were shipped by commercial carrier were released by the field sample custodian to the laboratory custodian receiving them. Evidence tape was placed on the shipping container over the joint between the container and the lid to indicate if tampering occurred during shipment. The tape was signed and dated by the field sample custodian. The seal was to be broken only by the lab custodian receiving the samples.

2.3.5.3 Shipping--

The shipping containers with samples remained in the field laboratory until the end of the test program. However, all coolers with solid waste, liquid waste, and ash samples were stored in the rear of the equipment truck in an attempt to reduce contamination of the field lab and for safety purposes. Packing material was arranged around the sample bottles in all of the shipping containers to prevent breakage during shipment.

At the end of the test program, the shipping containers were packed in a single layer in the rear of the equipment truck. The containers were arranged so that the samples remained stationary and in an upright position throughout the transport. During transport, the designated samples were kept at 4° to 6°C (39° to 43°F), adding ice to the coolers when necessary.

① ☐ Chain of Custody Record
② ☐ Traceability Log
③ Project Number _____
④ Date of Field Sampling _____
⑤ Location _____
⑥ Type of Sample _____
⑦ Container No. _____
⑧ Storage Requirements _____

⑨ Sample No.	⑩ Description	⑪ Other Ident.	⑫ Sampler	⑬ Inventory/ Level Check				⑭ Comments
			⑮ Date					

⑯ Seal Intact												
⑰ Date												
⑱ Checked by												

⑲ Relinquished by				
⑳ Date				
㉑ Time				
㉒ Received by				

Figure B-17. Traceability log.

2.4 SPECIFIC ABSORPTION TRAINS

The following subsections describe sampling and analysis procedures for specific absorption trains for isocyanates, phosgene, and chloride in stack gases. Collection of the sample was by liquid absorption or chemical reaction using a midget impinger collection train. The specific sorbent or reagent appropriate to the POHC of interest was placed in the impingers. As an alternative, the specific sorbent or reagent was incorporated into the MM5 train, provided the substitution did not interfere with collection of other POHCs. Absorption trains were used for continuous sampling, at sampling rates designed to obtain a sample as large as possible for analysis without exceeding the absorbing rate or capacity of the absorbing solution in the impingers.

2.4.1 Isocyanates in Stack Gas

Phenyl and methylene diisocyanate were the expected isocyanates in the stack gas at Upjohn. The sampling and analysis method used for collection of the isocyanates was based upon the NIOSH Manual of Analytical Methods, Volume 1, Method No.: P&CAM 141, "2,4 Toluenediisocyanate (TDI) in Air" (April 1977). This is a colorimetric method using a hydrochloric acid/acetic acid absorbing solution in a midget impinger collection train (see Figure B-18). The isocyanates are hydrolyzed by the absorbing solution to form the diamine derivative which is diazotized and coupled with N-(1-naphthyl)-ethylenediamine for analysis at 550 nm.

The sampling train had two midget impingers, each loaded with 15 mL of the absorbing solution. The stack gas was pulled through the train at 1 L/min for 20 min during each test run. At the end of the test run, the sample was returned to the field laboratory for on-site analysis. A Bausch & Lomb Spectronic 20 spectrophotometer with matched test tubes was used to measure the color developed.

Toluene diisocyanate was used as the standard material even though the expected isocyanates were phenyl and methylene diisocyanates. The absorbance of phenyl derivative was measured immediately after the reaction. The developed color from the sum of phenyl and methylene forms was present after a 1 hr waiting period, and the absorbance was also measured on the spectrophotometer.

2.4.2 Phosgene in Stack Gas

The sampling and analysis method used for collection of phosgene in stack gas at Upjohn was based upon NIOSH Manual of Analytical Methods, Volume 1, Method No.: P&CAM 219, "Phosgene in Air" (April 1977). This impinger collection method was chosen as the best available method for the collection of stack gas containing a low concentration of phosgene. Nitrobenzyl pyridine in diethyl phthalate was used as both the absorbing solution in the train and the color reagent. Stack gas samples were collected in a modified EPA Method 6 midget impinger train containing 10 mL of Freon 113 in the first impinger and 10 mL of the color reagent in each of the second

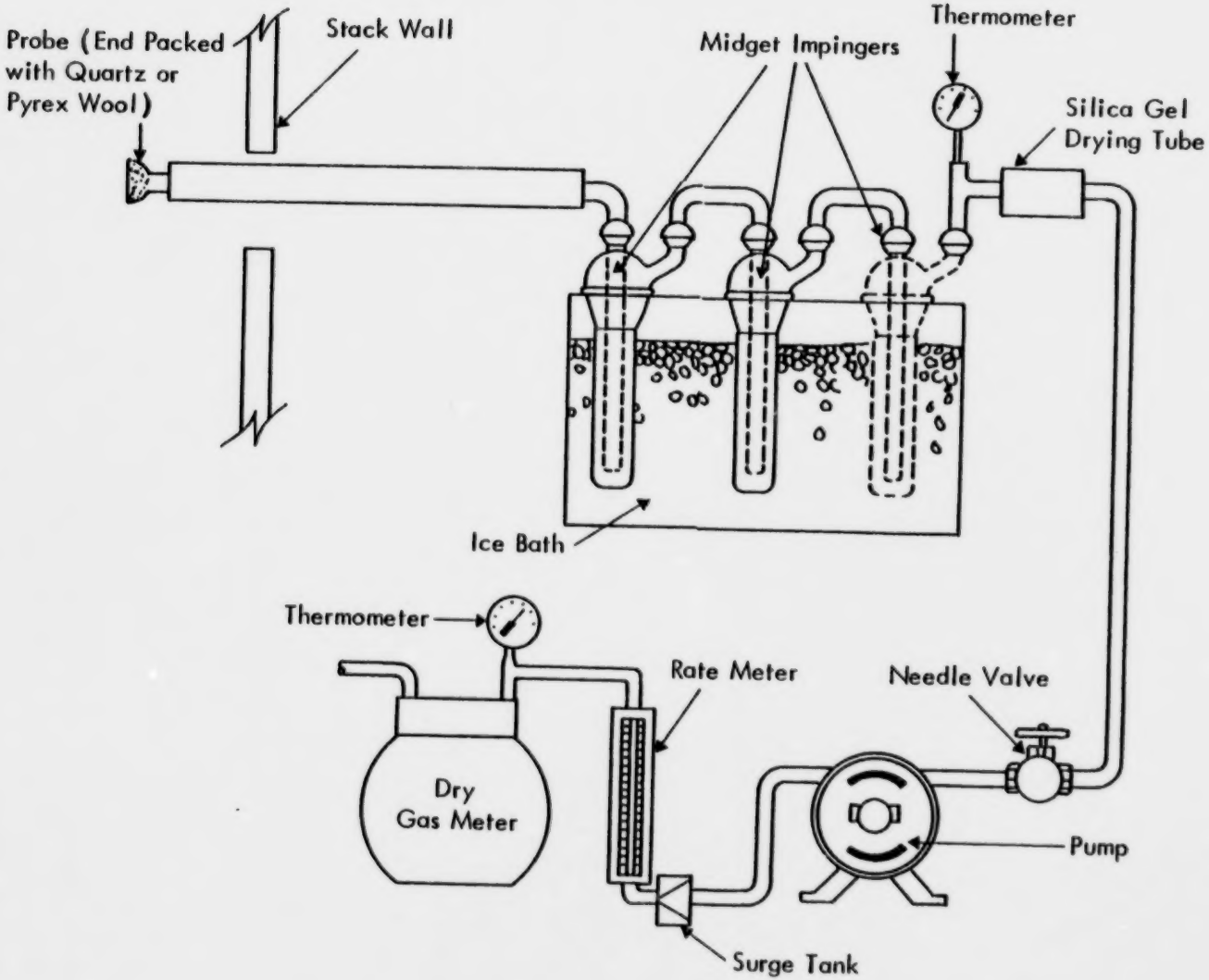


Figure B-18. TDI sampling train.

and third impingers (see Figure B-19). During each test run, the train was operated at 1 L/min for 50 min.

Following each test run, the sample was returned to the field lab for on-site analysis. The train was recovered and the sample was transferred to a cuvette for photometric measurement at 475 nm. A liquid standard of phosgene (1 mg/mL) dissolved in diethyl phthalate was prepared at the analytical lab and taken to the field site for subsequent dilution as a working standard.

2.4.3 Total Chloride in Stack Gas

The chloride emissions from the stack mainly as HCl were collected using the impinger collection method as part of the MM5 train. These aqueous samples were analyzed by following a colorimetric analytical procedure to determine total chloride.

2.4.3.1 Sampling--

A caustic solution was incorporated in one of the impingers of the MM5 train in order to collect HCl and other acidic gases in the stack gas. One hundred milliliters (100 mL) of 0.1 N KOH was placed in the third impinger (Greenburg-Smith design) of the MM5 train (see Figure B-1). Approximately 1.7 Nm^3 (60 dscf) of stack gas was collected at a sampling rate of 0.85 m^3/sec (0.5 cfm) for each test run. (The sampling and recovery procedures with the MM5 train are outlined in Section 1.0).

2.4.3.2 Analysis--

All aqueous samples from the MM5 train (KOH and condensate) were analyzed for chloride using EPA Method 325.2 as described in Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020. The procedure was a continuous flow automated colorimetric procedure. The thiocyanate ion was liberated from mercuric thiocyanate through sequestration of mercury by chloride ion to form unionized mercuric chloride. The thiocyanate ion then reacts with ferric ions to form a highly colored ferric thiocyanate which was measured at 480 nm. The system was spanned using a 200 μg/mL chloride standard and the chloride concentration is read directly.

Samples received from the field were first analyzed directly without dilution. Those samples with concentrations above the instrument range were serially diluted until they were within range. Samples that were cloudy or colored were run through the analytical system with the reagent line delivering deionized water to obtain a blank correction factor. This procedure rarely produced a significant correction.

Quality assurance audit samples were obtained in concentration ranges similar to the real sample. Therefore, serial dilutions were required to the same degree so that the audit included both dilution and analysis.

2.5 CONTINUOUS MONITORING

A continuous gas sample was extracted from a sampling point in the stack, conditioned, and simultaneously analyzed for oxygen, total hydrocarbons, carbon monoxide, and carbon dioxide as part of the evaluation of

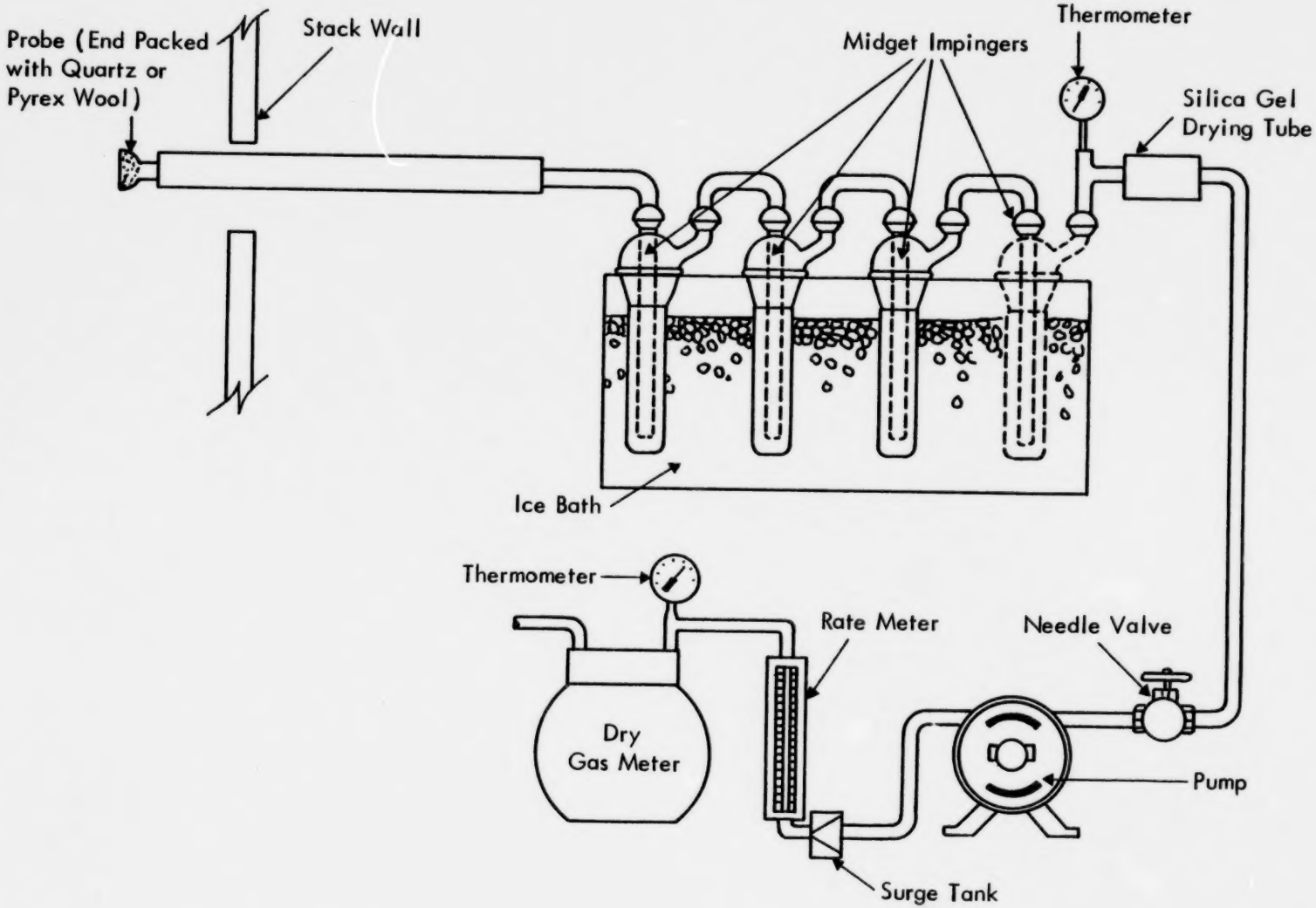


Figure B-19. Phosgene sampling train.

the combustion performance of the incinerator. Determination of carbon monoxide followed EPA Method 10 guidelines with the exception of the calibration procedure. Other instrumentation was used for determination of the other gases. Carbon dioxide was not monitored continuously in the gas stream at Zapata due to equipment scheduling problems.

2.5.1 Equipment

- Probe-sintered stainless steel of Inconel, 50 x 500 mm. The probe was fitted with a filter to eliminate particulate from the gas sample using either glass or quartz wool as the filter material.

- Sampling line - 200 ft of Technical Heaters, Inc., electrically heated Teflon line operating normally at 120°C (250°F).

- Conditioning manifold - MRI built with Permapure filter/coalescer and extractive dryer, Teflon diaphragm pump and capillary flow splitters to each analyzer (see Figure B-20). Inlet lines were heated before the dryer. Controls were provided also for probe blow-back and zero/calibration gas feed. The manifold included valving and calibrated rotameters for diluting stack gases as needed.

- Data recorders - Instrument outputs were recorded on individual strip chart recorders. Heath SR-204 recorders were used.

- Oxygen (O_2) analyzers (2) - Beckman models 742 and 7003 (Polarographic sensor).

- Total hydrocarbon (THC) analyzer - Beckman model 402 (heated oven flame ionization detector).

- Carbon monoxide (CO) analyzers (2) - Beckman model 215A and Horiba model PIR-2000L (nondispersive infrared) with silica gel interferences.

- Carbon dioxide (CO_2) analyzer - Horiba model PIR-2000S (nondispersive infrared).

- Instrument nominal ranges:

	Normal	Analyzer Span Limits
Oxygen	0 - 25%	1 - 25%
Carbon monoxide	0 - 1,000 ppm	100 - 10,000 ppm
Total hydrocarbons	0 - 25	5 - 25,000 ppm as propane
Carbon dioxide	0 - 15%	5 - 25%

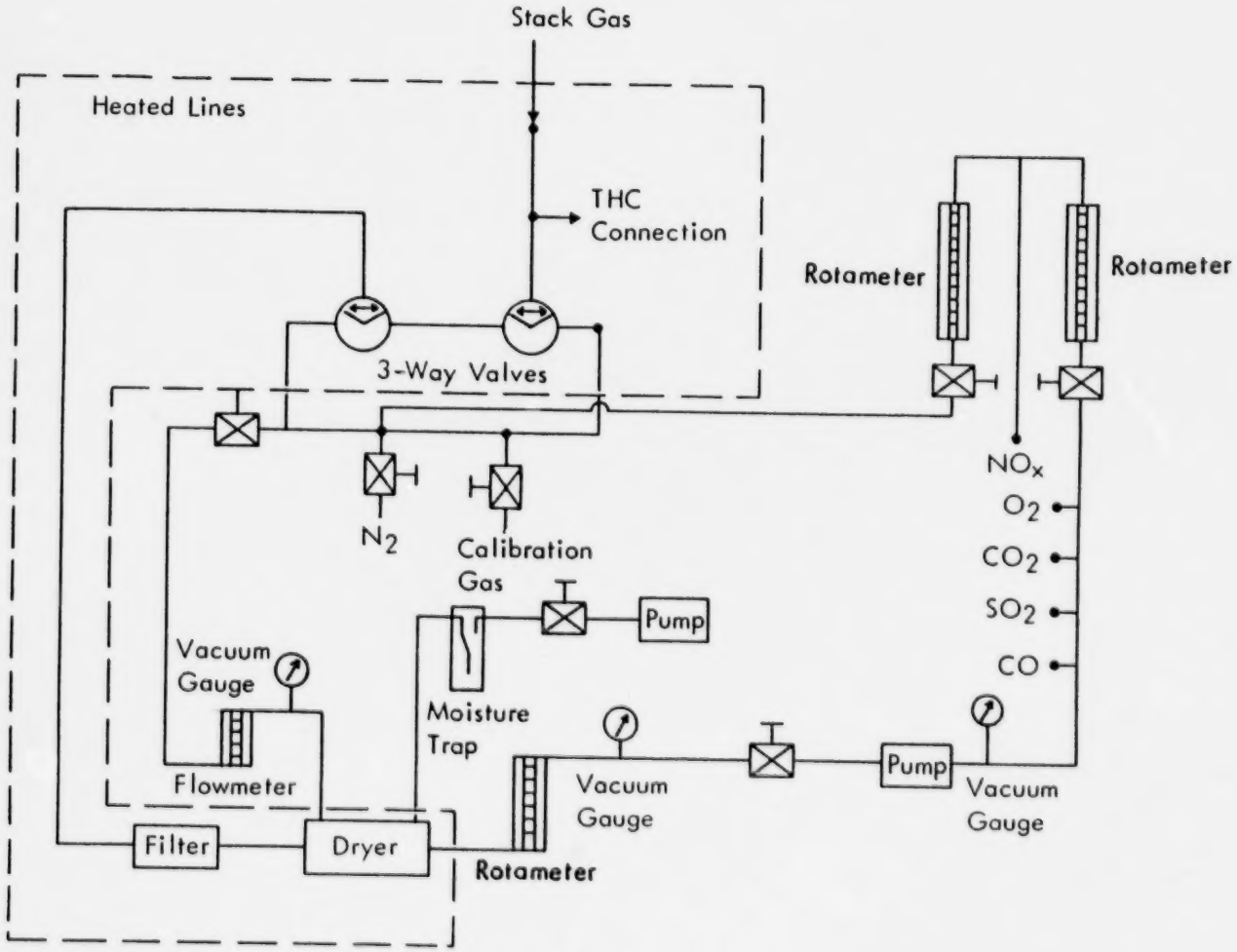


Figure B-20. Continuous monitor conditioning/dilution manifold.

2.5.2 Equipment Set Up

All field operating laboratory equipment including balances, fume hood, continuous monitors, and other special analyzers were installed in a portable leased lab trailer of appropriate size for each project. The heated Teflon line was used to connect the gas probe and the gas conditioning/dilution manifold. The probe was placed in the stack usually a few feet upstream from the MM5 sample ports. A warm-up period was required after the initial set-up of the instruments in order to stabilize the system (> 1 hr). An initial check of stack oxygen against a direct Fyrite measurement from the duct was used to determine gross sample line integrity prior to use for stack measurement.

2.5.3 Calibrations

A single point span and zero check for all analyzers was conducted at the start and end of each day according to manufacturer's guidelines. Span or zero drift of ≦ 10% was considered acceptable.

THC - Normally zeroed with burner air and spanned with propane in hydrocarbon-free air.

Carbon dioxide and carbon monoxide - Multicomponent mixtures at levels similar to stack concentrations with nitrogen balance gas for simultaneous span. Prepurified nitrogen was the zero gas.

Oxygen - Ambient air span and prepurified nitrogen as the zero gas.

Various single component span gases were on-hand for calibrating at different ranges. All calibration gases were supplied by Scott Specialty Gases.

2.5.4 Sampling

Normal sample flow into the conditioning manifold was 1 L/min and the flow into the THC analyzer was 4 L/min. The pressure drop through the line was monitored at the manifold for filter/line blockage. Steady increases in oxygen indicated line leakage.

The gas sample taken from the stack was conditioned by removing moisture, fine particulate, and other known interferences (i.e., CO_2 in the case of the CO analyzer). The conditioned gas was distributed to the various instruments via the manifold. The valving in the manifold system allowed instant switching from calibration to stack gas monitoring.

All analyzer data was recorded on individual strip chart recorders with manual reading taken every 15 min. The data were integrated over 1 min periods and entered into a computer program which converted chart readings to parts per million (ppm). Zero and span drift of the instruments was used to adjust the final concentrations of the gases.

2.6 SPIKING OF WASTE FEEDS

At six of the test sites, the organic waste feed line to the incinerator was spiked with carbon tetrachloride (CCl_4) and trichloroethylene (TCE). These plants included Ross, Plant B, Upjohn, Zapata, Mitchell, and TWI. A small injection system was designed and built for continuous injection of a spiking solution composed of a 50:50 mixture of CCl_4 and TCE. The solution was spiked into the organic waste feed line upstream of the location where grab samples of the waste feed were collected. The feed rate of the spiking solution was predetermined according to the individual test sites.

The injection system assembly was an all stainless steel apparatus with a positive displacement pump, monitored by a rotameter and a line pressure gauge. Safety features included check valves, line drains, and a pressure relief valve. At the beginning of each test, the system was calibrated by timing the solution being pumped into a graduated cylinder and recording the desired rotameter and pump vacuum settings. During each test run these settings were maintained in order to achieve a constant injection rate. The data were recorded periodically on a data sheet. At the completion of the test, the system was post-calibrated.

2.7 PROCESS MONITORING

At each test site one member of the field crew was assigned as process monitor. The process monitor ensured that normal operating conditions were established and maintained prior to and throughout each run. The process monitor was authorized to interrupt testing if specified conditions went outside of acceptable ranges or a plant upset or malfunction occurred.

All available process instrumentation was monitored and recorded during each run at every plant. The process monitoring included measuring level changes in liquid waste feed tanks and recording the weights of drums of solid waste fed during each run, to enable calculation of waste feed rates. At Upjohn, vent gas feed rate was monitored based on the plant flowmeter. Liquid waste feedrates at all but two plants were based on feed tank level measurements made by the process monitor. At Plant B and Du Pont the tank level readings were based on the plants level monitoring instruments.

In most cases, process readings from available plant instrumentation were recorded every half hour during each run. The process instrumentation available at each plant are listed in Table B-2. Data recorded from these instruments were used to compute average values for each run, which are contained in the individual plant reports in Appendices C through J.

2.8 VISIBLE EMISSIONS EVALUATION

At the plant's request, the plume opacity from the Upjohn incinerator stack outlet was determined visually by a qualified observer. The plume evaluation strictly adhered to the EPA Reference Method 9 guidelines and was conducted concurrently with the Modified Method 5 tests.

TABLE B-2. LIST OF PROCESS INSTRUMENTS MONITORED AT EACH PLANT

Ross	Plant B
Combustion chamber temperature	Organic waste tank level
Temperature exit dry quench	Aqueous waste tank level
Inlet temperature to 1st absorber	
Organic waste nozzle pressure	Organic waste feed rate
pH of 1st absorber effluent	Aqueous waste feed rate
IWS Nos. 1 and 2	Airflow to varporizer NG burner
AC volts	Airflow to flame port NG burner
AC amps	Waste airflow
DC kV	Flame port airflow
DC mA	
Spark rate	Atomizer temperature
	Vaporizer temperature
	Flame port temperature
	Oxidizer temperature
	Vaporizer pressure
	Oxidizer pressure
	Quench temperature
	Stack temperature
	Scrubber pressure drop
	Scrubber water recirculation flow
	Nos. 1 and 2 boilers
	Pressure drop
	Steam pressure
	Inlet temperature
	Outlet temperature
	Electrified filter bed
	Inlet temperature
	Exit temperature
	Pressure drop
	Fabric filter pressure drop
	Stonebed kV
	Stonebed mA
	Ionizer kV
	Ionizer mA

(continued)

TABLE B-2. (continued)

Upjohn	Zapata
Combustion chamber temperature	Main chamber temperature
Combustion chamber O_2 content	Second chamber outlet temperature
Liquid waste flow rate	
Vent gas flow rate	Main chamber pressure
Natural gas flow rate	
	Atomizing air pressure
Cooling spray water flow rate	Water flow rate to main chamber
Quench pot temperature	
Scrubber water flow rate	

American Cyanamid	Mitchell
Stack temperature	Lower chamber temperature
Feed pressure to nozzle	Upper chamber temperature
Atomozing steam pressure	
Combustion chamber pressure	Stack opacity
Feed tank pressure	

(continued)

TABLE B-2. (continued)

Du Pont

Liquid waste feed tank level
Liquid waste feed tank temperature

Kiln speed
Drum feed interval

1st stg. scrubber liquid temperature
2nd stg. scrubber liquid temperature
3rd stg. scrubber liquid temperature

Water outflow from plant

Natural gas volume (SCF)

1st stg. scrubber pressure
Makeup water inflow to 3rd stg. scrubber
Exhaust blower suction pressure
Exhaust blower suction temperature
Exhaust blower discharge temperature

Stack inlet temperature

Kiln

Atomizing airflow
Atomizing air pressure

Liquid waste pressure
Kiln pressure
Total airflow

Kiln exit temperature
Kiln exhaust O_2 concentration
Secondary airflow

Liquid waste feed rate
Combustion airflow

NG flow to afterburner
Second airflow to afterburner
Afterburner temperature

Kiln cyclone inlet temperature
Kiln pressure

Liquid incinerator

Atomizing airflow
Atomizing air pressure

Burner waste pressure
Incinerator pressure
Total airflow

Refractory temperature
Incinerator exhaust O_2 concentration

Liquid waste feed rate
Combustion airflow

Quencher pressure

(continued)

TABLE B-2. (concluded)

TWI
Lower chamber temperature
Upper chamber temperature
Temperature after prequench
CO concentration
O_2 concentration
Pressure drop across venturi
Pressure drop across mist pads
Water flow rate to venturi
Organic waste atomizing air pressure
Aqueous waste atomizing air pressure
Organic waste feed pressure
Aqueous waste feed pressure

An observation point was chosen at a distance sufficient to provide a clear view of the emissions with the sun oriented behind the observer in the 140-degree sector. The line of vision was perpendicular to the plume direction. Opacity readings were taken at the point of greatest opacity in that portion of the plume where condensed water vapor was no longer visible. The distance from the emission outlet to this point of observation in the plume was estimated. Evaluations were made and recorded to the nearest 5% at 15-sec intervals, in sets of 24 consecutive readings. In addition to recording opacity observations, a field record of weather conditions, sky conditions, plume description, and observer location in relation to the plume were recorded at the time the plume evaluations were initiated and completed.

The plume from the Upjohn incinerator could only be read during one of the three Modified Method 5 test runs due to overcast skies or darkness. Three sets of 6-min observations were taken concurrently with the second test run.

2.9 ROUTINE ANALYSES OF WASTE FEEDS AND ASH

Several routine waste feed and ash analyses were performed by outside laboratories. A summary of the types of analysis and the samples for which they were performed is included in Table B-3.

TABLE B-3. ANALYSIS PERFORMED BY OUTSIDE LABORATORY

Type of analysis	Reference No.[a]	Plant							
		Ross	Plant B	Upjohn	Zapata	American Cyanamid	Mitchell	Du Pont	TWI[b]
Liquid waste									
H_2O content	Karl Fischer[c]	X	X		X	X	X	X	X
Cl^- content	E442	X	X	X	X	X	X	X	X
Heating value	D240	X	X	X	X	X	X	X	X
Ash	D482	X	X	X	X	X	X	X	X
Viscosity	D88	X	X	X	X		X	X	X
Ultimate analysis	D3178	X	X		X		X	X	X
Solid waste									
H_2O content	Karl Fischer	X						X	X
Cl^- content	D2361	X						X	X
Heating value	D2015	X						X	X
Ash	D3174	X						X	X
Ultimate analysis	D3178	X						X	X
Ash									
Cl^- content	D2361		X			X			

[a] Reference number refers to American Society for Testing and Materials Standards (ASTM) method used in the analysis.

[b] TWI work was also analyzed for bromine.

[c] Water content was determined using Karl Fischer titration.

2.10 REFERENCES

1. Sterret, J. D., A. A. Barbin, J. W. Reece, W. G. Carter, and B. B. Ferguson. Contract No. 68-02-3215. Project Officer Dr. William J. Mitchell (MD-77), Environmental Monitoring Systems Laboratory, U.S. EPA, Research Triangle Park, North Carolina 27711.

2. U.S. Environmental Protection Agency. Test Methods for Evaluating Solid Waste - Physical/Chemical Methods, W-846, 2nd ed. July 1982.

3. Decker, C. E., and R. G. Hyland. U.S. Department of Health, Education, and Welfare, Public Health Service, Bureau of Disease Prevention and Environmental Control, National Center for Air Pollution Control, Cincinnati, Ohio, August 1967.

SECTION 3.0

LABORATORY ANALYTICAL METHODOLOGY

This section describes all aspects of the chemical analyses performed within the analytical laboratory including preparation of sample containers, receipt and control of the samples, sample preparation, sample analysis and data acquisition. Auxiliary activities include calibration procedure and frequency, data reduction, data reporting, data archiving, and preventative maintenance.

This section of the appendix begins with a discussion of sample control. Following are sections on calibration procedures for the major instruments, a review of the various analytical procedures used, and a discussion of data reduction, validation, reporting, and documentation. Finally, the section concludes with a description of the preventive maintenance program. References for the analytical section are found in subsection 3.6.

3.1 SAMPLE CONTROL

Adherence to strict sample traceability procedures was an extremely important aspect of this program because of the large number of samples and the importance of the data. Strict chain-of-custody was not followed for this program. However, strict sample traceability was followed which deviates from chain-of-custody only in that initials were allowed instead of full signatures during sample transfers and the samples were not required to be locked in a high security area. A special sample "log-in" office was used to receive, log-in, and distribute the samples.

3.1.1 Responsibility

It was the responsibility of the Analytical Task Leader to provide the Sample Control Office with notification forms detailing the imminent arrival of samples.

3.1.2 Sample Arrival Procedures

Upon receipt of the trial burn samples at the analytical laboratory, the following procedures were implemented:

- The coolers containing the samples were brought to the Sample Log-In Office by the sampling personnel.
- The samples were logged-in, if possible, the day of receipt.

- If there was insufficient time for log-in, the ice in the coolers was replenished, and the coolers were placed in locked laboratories overnight.

- The samples were logged-in the next day as described below. When possible, the sampling personnel assisted the sample control coordinator in unpacking and inspecting the samples and recording sample information in the Sample Log-In Laboratory Record Book (LRB).

3.1.3 Sample Log-In

Upon receipt of samples the sample control coordinator performed the following:

- Examined all samples for evidence of tampering, leakage, or other irregularities.

- Assigned a new number to each sample.

The following sample numbering system was used:

- The field sample number consisted of the following characters

  F 9000 - XX - YYY - Z

and provided the following information:

F	-	Field sample
9000	-	General project number
XX	-	Site or plant number (1 to 50 was used for the trial burn sites and 51 to 91 for the 40 site survey samples)
YYY	-	Sample number
Z	-	Replicate number of sample YYY

- The laboratory sample number was generated using the following characters:

  L 9000 - XX - YYY - Z - T - N

where:

- F (field) is changed to L (laboratory)

- T indicates the type of analysis to be performed on the sample according to:

-A- Volatile POHCs
-B- Semivolatile POHCs
-C- Metals
-D- EP toxicity herbicides and pesticides
-E- EP toxicity metals
-F- Other (heating value, water, chloride, and other parameters measured on a single sample by an outside testing laboratory)
-G- PCDD and PCDF

- N - replicate number of Sample T

Additionally, some of the samples were spiked. This was indicated by an 'S' following the designation for 'T'. For example, if three replicates of waste sample No. 2 from site No. 12 were to be analyzed for volatiles, the 3rd replicate was assigned the number,

F9000-12-2-A	S	3
Volatiles	Spike	Replicate No.

If the sample was to be also analyzed unspiked, in triplicate, the third replicate had the same number, except that there was no 'S'.

Three situations required special sample designations: (1) the identification used for laboratory composites; (2) the identification used for laboratory generated samples; and (3) the identification used for the 150-mL working extract from the waste feed extraction for semivolatiles.

For the first situation, an example of the identification and numbering for a laboratory composited sample is given below.

F 9000-02-003-1 (replicate 1 of waste sample No. 003). F 9000-02-006-3 (replicate 3 of waste sample No. 006). F 9000-02-007-2 (replicate 2 of waste sample No. 007).

The laboratory composite identification assigned to the resulting sample was LC 9000-02-500, followed by the appropriate designations for 'T' and 'N'. The 'C' following the 'L' indicated a laboratory composite. The 500 series number was assigned in chronological order, with each newly generated sample receiving a 500 + 1 number. American Cyanamid and TWI samples were assigned 900 and 500 series numbers, respectively, due to field samples previously assigned numbers in the 500 series. An important aspect of this sample identification was that the correct information on how the new composite sample was generated, and its assigned I.D. number, was recorded in the log-in LRB and on the sample Chain-of-Custody/Routing Form.

The second situation was the identification and numbering of laboratory generated samples including: method blanks, spikes, and blind samples. The identification assigned was L 9000-02-500, followed by the appropriate

designations for 'T' and 'N'. The 'L' indicated a laboratory sample and the 500 series indicated a laboratory generated sample. Again, the 500 series numbers were assigned in the same chronological order mentioned above, and the pertinent information on how the new sample was generated was recorded in the log-in LRB and on the sample Chain-of-Custody/Routing Form.

The third situation provided for the identification of the 50-mL working extract used in the semivolatile analysis of the waste feed samples. The unused portion of this extract was given the suffix RET which identified this extract as a sample to be retained. As an example, the identification was L 9000-02-101-1B-1 RET.

The sample information from the Sample Information Forms used by the sampling personnel was then recorded in the log-in LRB including the following:

- Original sample identification number
- Designated laboratory sample identification number
- Date of sample receipt
- Type of sample
- Other relevant sample information

A Chain-of-Custody/Routing Form was prepared in duplicate for each sample, including spikes and replicates. The original was sent with the sample and a copy was kept in the Sample Control Coordinator's file.

An improved Chain-of-Custody/Routing Form was implemented October 4 with the arrival of samples from Zapata. The earlier form, shown in Figure B-21, required one form for each sample and consequently generated burdensome paperwork for the laboratory personnel and the sample control coordinator. The improved form is shown in Figure B-22 followed by the form completion instructions. This form had a time-saving advantage in that up to eight samples could be tracked with one form. This method of sample tracking was made most effective by grouping like samples for laboratory routing.

3.1.4 Inventory Control

A given sample, such as a waste sample, could conceivably be split into triplicates for analysis of volatiles, into triplicates for analysis of semivolatiles, and into triplicates for analysis of metals. The analytical task leader informed the sample control coordinator in advance of such distribution of the sample so that chain-of-custody sheets for each sample were prepared to accompany the sample.

Form No. _____ Project No. _____

Midwest Research Institute
425 Volker Boulevard
Kansas City, Missouri 64110

SAMPLE CHAIN OF CUSTODY/ROUTING FORM

Field Identification Number: _____

Laboratory Identification Number: _____

Sample Type: _____

Sample to Be Analyzed For: (Volatiles/Semivolatiles/Metals (circle))

Other Analyses: _____

Duplicate Available: (Y/N) Duplicate Sample Number: _____

Original Container: _____

Storage Locations: _____

Special Instructions: _____

Background Information: _____

Required Sample Extraction Date: _____

Required Sample Analysis Date: _____

Laboratory/Area	Relinquished by: (signature)	Date/Time	Received by: (signature)	Date/Time
Log-in Office				
Sample Preparation				
Metals				
GC/MS				
Other (Identify)				

Notebook Reference Pages _____

Analyst Comments _____

_____

_____

_____

Figure B-21. Chain-of-custody form.

(See Back of Page for Explanation of Numbers)

LABORATORY CHAIN OF CUSTODY OR TRACEABILITY RECORD

① ☐ Chain of Custody Record
② ☐ Traceability Log
③ Project Number _____
④ Date of Laboratory Check-In _____
⑤ Location _____
⑥ Type of Samples _____
⑦ Container Type _____
⑧ Custody Office Storage Location _____

⑨ Laboratory Sample No.	⑩ Field Sample No.	⑪ Sample Description	⑫ Amount of Sample Removed (give date)	⑬ Comments

Laboratory/Area	⑭ Relinquished by: (signature)	⑮ Date/Time	⑯ Received by: (signature)	⑰ Date/Time
Custody Office				
Sample Preparation				
Metals				
GC/MS				
Other (Identify)				

⑱ Notebook Reference Pages [ ] ⑲ Notebook No. [ ]
⑳ Analyst Comments _____

Figure B-22. Improved chain-of-custody form.

FILLING OUT CHAIN OF CUSTODY/TRACEABILITY LOG

1. Check chain of custody or

2. Traceability log.

3. Enter project and task number.

4. Enter date samples were received by custody office.

5. Enter sampling location: plant name and/or city.

6. Enter type of sample, i.e., Tenax trap, condensate, bulk feed, etc. Record only one type of sample on a form.

7. Enter container type, i.e., Tenax trap, XAD trap, petri dish, narrow mouth quart bottle, 2-dram vial, 2 oz Rx bottle, etc.

8. Enter storage location samples will be taken from and returned to for custody office possession.

9. Enter laboratory sample number.

10. Enter field sample number.

11. Enter any additional sample description, i.e., hazards in handling the sample, appearance, Tenax trap number, etc.

12. Enter any amount of sample expended and date.

13. Enter any comments pertinent to the tracking of the entire sample, i.e., sample composited to form a new sample, sample transfer to a new custody form, sample split to give two or more items to keep in custody, sample lost, etc. Enter references to appropriate laboratory notebook (page and book number). If comments pertain to all samples listed, enter as "see time 20," and include these in the appropriate space provied at the bottom of the form.

14-17. Must be used to record a change in sample custodian following either chain of custody or traceability. Each time the custodian is changed, the samples must be inventoried using columns 9 and 11 through 13 and the transfer recorded using 14 through 17. Samples never change custody without being inventoried and signed off. The chain of custody record or traceability log must travel with the samples until transferred to the laboratory custodian.

18 and 19. Enter location of sample records listed in the project sample custodian's notebook.

20. Enter any comments pertaining to (a) an individual sample noted above (use footnote) or to (b) all the samples listed above. (See also item 13.)

Figure B-22. (continued)

The following is a summary of the inventory control procedures used:

- Each and every sample had a chain-of-custody sheet prior to transfer of the sample from the sample control coordinator to the appropriate analyst.

- If any sample was split, or otherwise subdivided, each of the subsamples also had a routing sheet. Sample splits had to be anticipated prior to sample distribution.

- All sample transfers were acknowledged by signing and dating the sample chain-of-custody sheet.

3.1.5 Document Control

Several different documents associated with the samples were generated throughout the project. The following document control procedures were followed:

- All sample documents and unused sample portions were returned to the sample control coordinator for filing and storage when the program was completed.

- The documents included the sample routing sheets, the subsample routing sheets, invoices, packing slips, etc.

- Tapes of GC/MS data were stored in a locked laboratory by the GC/MS facility manager.

- The information sheets were filed according to project number.

3.2 CALIBRATION PROCEDURES AND FREQUENCY

The major types of instruments that required calibration for this program were the mass spectrometers, the atomic absorption spectrophotometers (AAS), and the inductively coupled plasma emission spectrophotometer (ICP). The relevant aspects of the calibration procedures for these instruments are discussed below.

3.2.1 Mass Spectrometers

Both quadrupole (Finnigan 4000) and magnetic sector (Finnigan-MAT 311-A and Finnigan-MAT CH-4) mass spectrometers were used. Each of the instruments was calibrated: (a) at least on a daily basis; (b) if the mass spectrometer had been drastically retuned; or (c) if the mass range to be scanned was changed. The procedures used are described below.

3.2.1.1 Finnigan 4000--

1. Introduce the calibration compound, perfluorotributylamine (FC-43), into the ion source with the Ionizer Mode in the EI/SEP position and the electronics module in manual control.

2. Set the oscilloscope for split screen display. Adjust until masses 181 and 414 are centered in the two half-screens.

3. Adjust the quad offset, offset program, and lens voltages until the 181:414 ratio is approximately 2:1 or less.

4. Set the multiplier to between 1,350 and 2,000 V. Choose a preamp setting to obtain a signal of 6 to 12 V for mass 69. A high signal (12 V) is needed for scan rates faster than 3 sec.

5. Switch the quadrupole electronics module from manual to computer control.

6. Set up an acquisition from the computer terminal. The program command to acquire data is "ACQU." Subcommands in ACQU that should be set are M (minimum area to acquire), W (minimum peak width), and T (threshold). These subcommands can be set with values appropriate for the analysis.

7. Acquire at least five scane for calibration. When the acquisition is complete, turn off the supply of FC-43 to the ion source

8. Calibrate a scan from the run. The scan to be calibrated is user defined.

9. Determine whether the scan calibrated is acceptable. The instrument is now ready for sample analysis.

3.2.1.2 Finnigan-MAT 311-A--

1. Introduce the calibration compounds, perfluorokerosene (PFK), into the ion source via the reference inlet (180°C).

2. With the magnet control in either "Field" or "Current" control bring a characteristic PFK peak into focus on the center of the oscilloscope display.

3. Maximize ion optics voltages to maintain a symmetrical peak shape with maximum intensity.

4. Via the computer (MS scan under computer control), input desired mass scan mode and range. Set multiplier to between -1,300 and -2,000 V. Set filter to appropriate setting.

5. Set up an acquisition from the computer terminal. The program command to acquire data is "ACQU." Subcommands in ACQU that should be set are M (minimum area to acquire), W (minimum peak width), and T (threshold). These subcommands can be set with values appropriate for the analyses.

6. Acquire at least five scans for calibration. When the acquisition is complete, turn off the supply of PFK to the ion source.

7. Calibrate a scan from the acquisition using the program command "CALI."

8. Determine whether the scan calibrated is acceptable. The mass spectrometer is now ready for sample analysis.

3.2.1.3 Finnigan-MAT CH-4

1. Introduce the calibration compound, perfluorokerosene (PFK), into the ion source via the heated gas inlet system.

2. With the magnet in manual control bring a characteristic PFK peak into focus on the oscilloscipe with the accelerating voltage in the fastest sweep mode.

3. Maximize ion optics voltages to maintain a symmetrical peak shape with maximum intensity.

4. Via the computer (MS scan under computer control), input desired mass scan mode and range. Set multiplier to between -1,300 and -2,000 V. Set filter to appropriate setting.

5. Set up an acquisition from the computer terminal. The program command to acquire data is "ACQU." Subcommands in ACQU that should be set are M (minimum area to acquire), W (minimum peak width), and T (threshold). These subcommands can be set with values appropriate for the analyses.

6. Acquire at least five scane for calibration. When the acquisition is complete, turn off the supply of PFK to the ion source.

7. Calibrate a scan from the acquisition using the program command "CALI."

8. Determine whether the scan calibrated is acceptable. The mass spectrometer is now ready for sample analysis.

3.2.2 <u>AAS and ICP</u>

1. Each instrument was calibrated at least daily and once every time a new batch of samples was analyzed.

2. For ICP emission spectrometry, an Instrument Check Standard (ICS) was analyzed after calibration according to Jarrell-Ash instrument operating procedures. If the measured concentration values for the analytes of the ICS were within ±5% of the correct values, samples were then analyzed. If not, the instrument was recalibrated.

3. For atomic absorption analysis, four calibration standards, and a reagent blank were analyzed in triplicate. A linear regression of the absorbance values versus standard concentration was performed. If the coefficient of determination (r^2) was $\geqq 0.996$, the calibration curve was sufficiently linear and sample analysis was begun. Otherwise, instrument calibration was repeated.

3.3 ANALYTICAL PROCEDURES

A large variety of analytical techniques were used to accomplish the data requirements for this program with GC/MS as the primary technique for POHC determinations. This section of the manual describes the details of all aspects of the analytical techniques. The areas covered include:

- Glassware preparation
- Waste sample homogenization and aliquoting
- Sample fortification (spiking)
- Sample extraction
- Sample digestion (preparation for metals analysis)
- Sample extract drying and concentration
- Preparation and use of surrogate, internal, and calibration standards
- GC/MS analysis of methylene chloride extracts
- GC/MS data retrieval
- Extraction Procedure toxicity testing
- AAS analysis of metals
- ICP analysis of metals

3.3.1 Glassware Preparation

3.3.1.1 Glassware (Major Items) Needed for Field Sampling--
The glassware was prepared by the analytical chemists for use by the field sampling crew and included the following items (the use and the typical number needed per incineration test site are given in parentheses).

- One-quart wide-mouth jars with Teflon-lined caps (collection of nonliquid waste samples and bottom ash samples; 6 per incineration test).

- One-liter glass bottles with Teflon-lined caps (collection of liquid waste samples; 6 per incineration test).

- Forty-milliliter volatile organic analysis (VOA) vials (collection of duplicate aqueous samples for analysis of volatiles and collection of duplicate integrated waste feed samples; 60 per incineration test).

- Two-liter glass bottles with Teflon-lined caps (collection of aqueous samples; 12 per incineration test).

- Condensers (6 per incineration test).

- XAD-2 adsorbent traps (16 per incineration test).

- Tenax and Tenax/charcoal adsorbent traps (21 each per incineration test, loaded into leak-tight carriers).

3.3.1.2 Glassware Cleaning--

Detection limits as low as 2 ng per analysis were required for POHCs in some of the samples; thus the importance of clean glassware could not be overemphasized. Slightly different techniques were required for preparation of glassware for analysis of organic and metal species. Bottles for collection of aqueous samples to be analyzed for both organic and metal species incorporated the procedures for both types of glassware as described below:

3.3.1.2.1 Glassware for organic analysis--

- Wash all glassware in hot, soapy water (use ISOCLEAN nonionic soap and a clean brush).

- Rinse with tap water, distilled water, and distilled-in-glass methanol.

- Place glassware into a clean glassware drying oven set at 110°C and allow to dry for at least 1 hr.

- Remove glassware from drying oven and immediately cover open ends with precleaned heavy-duty aluminum foil or Teflon-lined caps.

- Any glassware that gave an indication of still being dirty, i.e., the water and methanol rinses did not 'sheet', was recleaned by soaking in concentrated sulfuric acid or "NOCHROMIX" cleaning solution.

3.3.1.2.2 Sample vessel preparation for metals (digestion/leaching)--

Glass tubes:

1. Wash glass tubes and caps in detergent.
2. Rinse and soak tubes in 8N (reagent grade) NHO_3 overnight. Then fill with Milli-Q, add 1 mL HNO_3 (Ultrex®) and soak overnight.
3. Soak tube caps in Milli-Q water to which 1 to 2 mL Ultrex® has been added. Soak overnight.
4. After tubes and caps have soaked, rinse with Milli-Q water. Drain if possible.

Clean beakers:

1. Fill beakers half full with 8N NHO_3 (reagent grade).
2. Cover with a clean watch glass.
3. Reflux 2 hr.
4. Drain and rinse with Milli-Q water.

Teflon jars:

1. Add 8 to 10 mL HNO_3 (reagent) to vessel (clean).
2. Cap tightly and place in 100°C oven for 2 hr.
3. Cool and drain.
4. Rinse with Milli-Q water.

Polyethylene plastic bottles:

1. Add Milli-Q water to clean plastic bottles.
2. Add 1 mL concentration HNO_3 (Ultrex®).
3. Allow to soak overnight.
4. Rinse with Milli-Q water.

Filter papers:

1. Fold No. 41 Whatman paper and place in plastic funnel.
2. Pass 100 mL 1% HNO_3 (Ultrex®) through filter.
3. Follow with rinse of 150 mL Milli-Q water.

3.3.2 Waste Feed/Kiln Ash Sample Homogenization and Aliquoting

It was extremely crucial that all waste feed and kiln ash samples were homogenized as completely as possible prior to aliquoting, spiking, and analysis. Since the waste feed samples were, in most cases, liquids, the worst case scenario was homogenizing a multi-phased liquid. However, some solids which were associated with the samples also had to be broken up and dispersed as well as possible throughout the sample.

Waste samples were analyzed from all the incineration trial burns. The number of sample aliquots required for the different types of analyses

(volatiles, semivolatiles, and metals) and replicates was determined prior to sample homogenization so that all of the correct size aliquots were removed immediately following sample homogenization.

3.3.2.1 Waste Feed Kiln Ash Sample Observation--

The waste or kiln ash samples were first carefully observed in order to determine the expected degree of difficulty in homogenizing the samples. One of two alternative homogenization techniques was used.

3.3.2.2 Sample Homogenization--

3.3.2.2.1 Manual homogenization--Most samples were able to be homogenized using vigorous shaking of the sample container followed by stirring with a stirring rod.

3.3.2.2.2 Mechanical homogenization--Waste samples which could not be readily homogenized using a mechanical mixer, such as an Eberbach Corporation stainless steel 250-mL semi-micro blender that fit onto a commercial Waring blender base. The waste sample and the mechanical mixer were first cooled so that loss of volatiles was minimized during mixing. The entire contents of one of the waste feed sample containers (i.e., 40-mL screw-cap vial) was then added to the mechanical mixing device and mixed for 1 min. Samples to be analyzed for metals were mixed in a glass blender container. Although it was convenient to homogenize the entire contents of a 40-mL replicate vial sample, beginning with the Mitchell test only the 1-L sample bottles were used for waste sample analysis because the 40-mL replicate samples may not have been representative of the waste in the 1-L bottles.

3.3.2.3 Sample Aliquoting--

Immediately following sample homogenization the appropriate size, e.g., 2.0 mL or 2.0 g, and number of replicate samples were removed from the mixed sample and added to the appropriate sample extraction and/or digestion glassware as described in Subsections 3.3.4, 3.3.5, and 3.3.7.

3.3.3 Sample Fortification (Spiking)

Most of the samples analyzed for this program were fortified with organic comopunds, and in some cases metals, in order to determine if any matrix effects or sample extraction procedures caused poor recovery (and thus poor accuracy) in quantifying native sample components. Organic surrogate recovery compounds were spiked into all samples at known concentrations prior to sample extraction and analysis. Selected samples were spiked with POHCs at a level 1 to 5 times the native level detected from analysis of the unspiked sample. Some POHCs not detected in the unspiked samples were spiked at levels near the estimated detection limit to determine if the compound would have been detected if it had been present at a low level in the sample. These detection limit levels were about 100 to 200 μg/g for waste feed samples, 2 to 5 μg/L for aqueous samples, and 1 to 2 μg for XAD-2 resin and air particulate filter/probe rinse residue samples.

Since the extracts from the XAD-2 resin and the condensate water were composited prior to GC/MS analysis, each of these two samples were spiked with only one surrogate compound.

The organic spiking procedures described below apply to both volatile and semivolatile surrogate and POHC organic compounds. However, only semivolatile POHCs were analyzed on XAD-2 resins, in MM5 condensate water, and on air particulate filter/probe rinse residue samples. The volatile and semivolatile spiking compounds were also contained in different solutions and spiked into different aliquots of the sample. The volatile spiking solutions were prepared in methanol and the semivolatile spiking solutions were prepared in methylene chloride, methanol, or methylene chloride/toluene depending on the solubility of the compounds.

The metal fortifications were performed on samples which were prepared and analyzed at the same time as the unspiked samples (there are not metal surrogate compounds). Because the spiking was performed on samples whose native level was not known, some of the spike levels did not fall within the 1 to 5 times the native level.

3.3.3.1 Waste Feed Fortification--

Separate aliquots of all homogenized waste feed samples were spiked with solution injected as close as possible to the center of the weighed aliquots of the waste feed sample and allowed to equilibrate with the sample for 10 min prior to solvent extraction. For samples which were spiked with POHCs following determination of the native POHC level, the aliquots were also weighed out immediately following homogenization of the samples. Two-gram aliquots of the samples for later spiking with volatile POHCs were stored at 4°C in 2-mL GC vials to prevent loss of native volatile components.

The spiking level that was generally used for the surrogate compounds was 500 μg of each volatile surrogate in 2 g of sample (250 μg/g) and 1,250 μg of each semivolatile surrogate in 5 g of sample (250 μg/g).

3.3.3.2 XAD-2 Resin Fortification--

The front and back XAD-2 resin samples and blanks were spiked with a surrogate compound (decafluorobiphenyl) at the 20 μg level. The XAD-2 resin was spiked by injecting the solutions of the surrogate into the center of the resin in a volume of 1.0 mL of methylene chloride. The syringe needle was moved about so that all of the compound were not deposited in one spot on the resin. Other portions of XAD-2 resin were spiked with POHCs to determine recoveries.

3.3.3.3 Air Particulate Filter/Probe Rinse Residue Fortification--

Air particulate filters may be the most difficult sample matrix to spike accurately because a portion of the spiked compounds could evaporate along with the spiking solvent since there are no adsorptive forces in effect to hold the spiked compounds onto the filter. However, since it is unlikely that hot air particulate filters collect any compounds except for relatively high molecular weight semivolatile compounds, only the relatively high molecular weight compounds, which would not readily evaporate from a

spiked filter, were used for spiking. The only surrogate compound used for spiking was the D_{12}-chrysene surrogate at the 20-μg level.

The air particulate filter was spiked with the surrogate by adding the D_{12}-chrysene in 50 μL of solvent. The solvent was distributed over most of the surface of the filter, and care was taken not to let any of the solvent drip through the filter or contact another surface which would cause loss of the spiked analytes.

3.3.3.4 Aqueous Samples--

Aqueous samples were spiked by injecting a solution(s) of the surrogate compounds into separate aliquots of the water for analysis of semivolatile and volatile compounds. The semivolatile surrogates were D_8-naphthalene, D_{12}-chrysene, and decafluorobiphenyl at the 20 μg/L level. The sample was then gently swirled to effect mixing. Aqueous samples spiked with volatile organic compounds were stored in 40-mL screw-cap sample vials with zero headspace at 4°C in order to prevent losses of the volatile analytes.

3.3.3.5 Fortification of Metals--

The various types of samples were spiked with metal analytes using a calibrated pipet to disperse the acidic, aqueous standard. The samples were then allowed to equilibrate and digested using the procedures described in subsection 3.3.7.

3.3.4 Waste Feed Sample Extraction for Analysis of Volatiles

The solvent for extraction and analysis of volatile POHCs in waste samples was tetraglyme. Tetraglyme is a very good solvent for organic compounds and is soluble in water so that an aliquot of the tetraglyme extract can be added to water and this step immediately followed by a purge-trap-desorb GC/MS analysis of the sample.

3.3.4.1 Extraction with Tetraglyme--

1. Add 40 mL of reagent tetraglyme to a 50-mL culture bottle.

2. Weigh capped tube on an analytical balance. Record weight in LRB.

3. Weight about 2 g weight of freshly homogenized sample into a 2-mL GC vial, spike with surrogate compounds, cap, rehomogenize, and allow sample to equilibrate for 10 min.

4. Add, as quickly as possible to minimize loss of volatiles from the sample, the spiked sample to the tetragylme such that the sample is dispersed or immersed in the tetraglyme as quickly as possible.

5. Cap and reweigh the sample. Record weight in LRB.

6. Disperse the sample with vigorous agitation for 1 min (sonify the mixture if necessary).

7. Obtain clear supernatant by letting stand, or centrifuging, if necessary.

8. Remove a 1.0 mL aliquot of the sample and transfer to a GC vial.

9. Submit sample for GC/MS analysis.

3.3.5 Waste Feed Extraction for Analysis of Semivolatiles

The waste feed/kiln ash samples were extracted with methylene chloride. To ensure that acidic and basic compounds were not lost because of the presence of solvent--insoluble salts, the pH of the sample was adjusted to 7. Also, the water in the samples was bound with anhydrous sodium sulfate. The sample was screened by GC/FID to achieve optimum concentration for GC/MS analysis.

3.3.5.1 Extraction of Waste Feed Samples with Methylene Chloride--

1. Tare an empty, uncapped 200-mL culture bottle on a top-loading electronic balance.

2. With bottle on the balance, quickly add 2.0 or 5.0 g of waste (predetermined by the nature and estimated semivolatile organic content of the waste), and record the sample weight in the LRB. Cap the bottle.

3. Open the bottle briefly to spike the surrogate standard directly into the center region of the waste material. The standard solution injected contained 1,250 μg each of D_{12}-chrysene, decafluorobiphenyl and D_8-naphthalene. Recap, gently swirl, and let bottle stand for 10 min to allow solution to disperse into the sample.

4. Add 50 mL of methylene chloride and extract the sample with vigorous agitation for 1 min (sonify the mixture to achieve dispersion if necessary).

5. If a water layer forms on the top of the methylene chloride, measure the pH by immersing a glass rod into the aqueous layer and touching it to a piece of multi-range pH paper.

6. If the pH is acidic, add several drops of 0.4 M K_3PO_4, shake, and recheck pH. Repeat until aqueous phase is neutral.

7. If the pH is alkaline, add several drops of 0.4 M H_3PO_4, shake, and recheck pH. Repeat until aqueous phase is neutral.

8. Add 15 g of anhydrous sodium sulfate, cap, and shake vigorously for 2 min.

9. Add 100 mL methylene chloride, cap, and shake vigorously for 1 to 2 min.

10. Obtain a particulate-free supernatant by letting the sample stand.

3.3.5.2 Extraction of Kiln Ash with Methylene Chloride--

1. Set up a §55/50 Soxhlet extraction apparatus with 200 mL of methylene chloride in a 250-mL round bottom boiling flask along with several boiling chips.

2. Place 25.0 or 50.0 g of kiln ash into thimble filter and position filter in the Soxhlet extractor.

3. Spike 1,000 μg of D_8-naphthalene, decafluorobiphenyl, and D_{12}-chrysene into the center region of the sample.

4. Soxhlet extract the ash sample for at least 16 hr.

5. Dry the extract with sodium sulfate.

6. Concentrate extract to approximately 1.0 mL using Kuderna-Danish (K-D) evaporation.

7. Proceed to screening by GC/FID.

3.3.5.3 Screening by GC/FID--

Because it was not possible to accurately predict the concentration of the semivolatile organics in the methylene chloride extracts, it was necessary to screen the extract using a GC/FID analysis. Failure to do so could result in a severely saturated GC/MS peaks which would necessitate shutdown of the GC/MS and also result in obtaining no useful data from that GC/MS run. Alternatively, the concentration of the components could be so low that few, if any, compounds would be observed. In either case, the sample extract was appropriately concentrated or diluted prior to GC/MS analysis.

1. Analyze 1.0 μL of the methylene chloride extract obtained in 3.3.5.1 and 3.3.5.2 by gas chromatography using the following conditions:

Detector: Flame ionization (FID)

Column: 1.8 m x 2 mm ID glass column packed with 3% SP-2250, 50% phenyl methyl silicone

Column temperature: 30° to 40°C (4-min hold), then 8°C/min to 255°C (10-min hold)

Column flow: 30 cm/s linear velocity (He)

Injection temperature: 280°C

Detector temperature: 300°C

Injection: Grob-type, splitless with 30-sec split time

2. From inspection of the resulting GC/FID chromatogram, estimate the amount of sample extract concentration required so that the average peak

height of the five largest peaks corresponds to about 50 ng as determined from GC/FID analysis of a 50 ng/μL external surrogate calibration standard.

3. Concentrate, using K-D evaporation, an aliquot of the methylene chloride extract to an appropriate final volume.

4. If necessary, dilute or concentrate a portion of the methylene chloride extract and bring to 1.0 mL volume.

5. If greater than a 10 x dilution is necessary, reanalyze the extract by GC/FID to confirm the correct concentration range.

6. Place extracts in a GC vial at 1.0 mL.

7. Spike all extracts with 50 μg of decafluorotriphenyl phosphine (DFTPP) (to monitor relative ion abundance) and submit for GC/MS analysis.

3.3.6 Sample Train and Aqueous Sample Extraction for Semivolatiles

The components of the MM5 sampling train that needed to be extracted were the:

- Air particulate filter/probe rinse residue
- XAD-2 resins (2)
- Condensate water

Since the extracts from the XAD-2 samples were composited prior to GC/MS analysis, each of these samples was spiked with only one surrogate compound.

The additional aqueous samples from the trial burns that were spiked with all three surrogate compounds (D_8-naphthalene, decafluorobiphenyl, and D_{12}-chrysene) and extracted were the scrubber water, quench water, and bottom ash. If the bottom ash also contained a solid component, it was extracted in the same manner as described below for the XAD-2 resin following decantation of the water. The rinse sample from the MM5 train was evaporated to dryness, and the residue weight determined by the sampling personnel. This residue was Soxhlet extracted together with the air particulate filter. Generally, the extracts from all the sampling train components (XAD-2 resins, filter/probe rinse residue, and condensate water) were combined into a single extract for analysis thus generating a new sample, as described below. In some cases, the extracts were analyzed separately in order to determine the distribution of compounds among the different components of the sampling train.

3.3.6.1 Extraction of Air Particulate Filter/Probe Rinse Residues--
The air particulate filters were Soxhlet extracted with methylene chloride.

1. Set up a § 55/50 Soxhlet extraction apparatus with 200 mL of methylene chloride in a 250-mL round-bottom flask along with several boiling chips.

2. Spike the sample with 20 μg of the D_{12}-chrysene surrogate compound.

3. Add the sample to the Soxhlet extractor with tweezers being careful not to allow any particulate material to be lost from the filter.

4. Soxhlet-extract the filter/probe rinse residue sample for at least 16 hr.

5. Dry the extract with sodium sulfate and concentrate to 1.0 mL.

6. Transfer extract to GC vial, spike with 20 μg of DFTPP, and submit for GC/MS analysis.

3.3.6.2 Extraction of XAD-2 Resins--

The MM5 sampling train for POHC sampling contained two separate XAD-2 resin traps each containing 75 g of XAD-2 resin. The first trap was usually very wet because stack gas condensate passed through it during sampling. The XAD-2 resin in the backup trap was not as wet because it was located downstream from a condensate reservoir. Generally the samples were extracted separately.

1. Set up two § 71/60 Soxhlet extractors with a § 29/42 joint attached to a 1,000 mL round-bottom flask containing 600 mL of methylene chloride and several boiling chips.

2. Add the 75 g of XAD-2 resin from each of the two collection traps to separate Soxhlet extractors. Use precleaned glass wool to hold the XAD-2 resin in the Soxhlet extractor. Soxhlet extractors should not be filled more than one-half full with resin.

3. Spike the front XAD-2 resin samples with 20 μg of decafluorobiphenyl surrogate compound.

4. Soxhlet-extract the resin for at least 16 hr.

5. If the methylene chloride extract in the round-bottom flask develops an aqueous layer on top of the methylene chloride layer, remove the water using a 2,000 mL separatory funnel.

6. Drain the methylene chloride extract back into the round-bottom flask and save for combining with the condensate water extract.

3.3.6.3 Extraction of Aqueous Samples (MM5) Train Condensate, Scrubber Effluent, Quench Water, and Bottom Ash Liquid--

Each of the aqueous samples was extracted with methylene chloride according to EPA Method 625[1] using the technique described below. The condensate water extract from the MM5 train was combined with the extracts from the XAD-2 and filter/probe rinse residue. The scrubber effluent, quench

water, and bottom ash extracts were dried, concentrated, and analyzed by GC/MS as separate samples.

1. To extract the MM5 train condensate use a 2,000-mL separatory funnel.

2. Add 1.0 L or total condensate available (record volume in LRB) to the 2,000-mL separatory funnel.

3. Spike the MM5 condensate water with 20 μg of the D_8-naphthalene surrogate compound. Spike the other aqueous samples with 20 μg of all three surrogate compounds.

4. Check the pH of the aqueous sample using a glass stirring rod and multi-range pH paper.

5. Adjust the pH to about 7 using 6 N sodium hydroxide for acidic samples or 6 N hydrochloric acid for alkaline samples. Add acid or base, swirl contents of separatory funnel, check pH, and repeat as necessary until a neutral pH is attained. However, if any acidic compounds are known to be POHCs in the sample, adjust the pH to 2 to 3 and if any basic compounds are known to be POHCs in the sample, adjust the pH to 10 to 11 prior to extraction.

6. Add 60 mL of methylene chloride to the sample bottle, cap and shake 30 sec to rinse the walls.

7. Transfer the methylene chloride to the separatory funnel and extract the sample by vigorously shaking the funnel for 2 min with periodic venting to release excess vapor pressure.

8. Allow the organic layer to separate from the water phase for a minimum of 10 min. Drain the methylene chloride extract into a 250-mL Erlenmeyer flask.

9. Add a second 60-mL volume of methylene chloride to the sample bottle and complete the extraction procedure a second time, combining the extracts in the Erlenmeyer flask.

10. Perform a third extraction with 60 mL of methylene chloride and combine extracts in the Erlenmeyer flask.

11. Combine the extracts from the MM5 sampling train condensate with the XAD-2 extract to yield a composite sample.

3.3.7 Methylene Chloride Extract Drying and Concentration

Each of the methylene chloride extracts was dried and concentrated for GC/MS analysis as described below.

1. Pour the combined methylene chloride extract through a drying column containing 3 to 4 in. of powdered anhydrous sodium sulfate which has

been prepurified using Soxhlet extraction with methylene chloride, dried, and heated in a muffle furnace at 400°C.

2. Collect the dried extract in a 500-mL K-D flask equipped with a 10-mL concentrator tube.

3. Rinse the original extract sample container with 40 mL of methylene chloride, pour through the drying column, and combine with the dried extract.

4. Add two clean boiling chips to the flask and attach a three-ball macro-Snyder column.

5. Prewet the Snyder column by adding about 1-mL methylene chloride through the top.

6. Place the K-D apparatus on a hot-water bath (60° to 65°C) so that the concentrator tube is partially immersed in the water, and the entire lower rounded surface of the flask is bathed with water vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 min.

7. Concentrate the extract to near, but not complete, dryness. The extract must be watched very carefully at this point.

8. Remove the K-D apparatus from the hot water bath and allow the solvent to drain for at least 10 min during cooling.

9. Rinse the walls of the receiver with 1 mL of methylene chloride using a 1-mL syringe.

10. Attach a condensate tower to the receiver and concentrate the extract to about 0.6 mL under a gentle stream of purified nitrogen.

11. Transfer the extract and sufficient washings to a GC vial to yield a final volume of 1.0 mL.

12. Spike sample with 20 μg of DFTPP and submit for GC/MS analysis.

3.3.8 Sample Digestion/Leaching (Preparation for Metals Analysis)

The three types of samples that needed to be digested and/or leached and then analyzed for metals were the waste feed samples, air particulate filter/probe rinse residues, and in some cases, the aqueous silver catalyzed persulfate impingers from the MM5 train.

3.3.8.1 Waste Feed Samples--
To analyze the waste feed samples for metals:

1. Weigh 1 g of sample into an acid-cleaned tared, 60-mL screw-cap glass tube.

2. Wrap the threads of the tube with Teflon tape to serve as a seal.

3. Add 10 mL 8 N Baker Ultrex® HNO_3 to the sample.

4. Cover the tubes with loosely fitted screw caps and heat for 4 hr at 60°C in a hot air oven.

5. After the samples have predigested, tighten the screw caps and heat the tubes for 8 hr at 125°C. Cool the tubes to room temperature and add 10 mL of 10% (v/v) Baker Ultrex® HNO_3 and recap the tubes.

6. Vigorously shake the capped tubes by hand and allow the phases to settle.

7. Filter the sample through a precleaned No. 41 Whatman paper into a tared 30-mL plastic bottle.

8. Add on additional 10 mL of 10% HNO_3 to the tube, shake, and add to the filter.

9. Record final mass.

3.3.8.2 Air Particulate Filter/Probe Rinse Residues--
The metals analysis digestion procedure for particulates on a segment of the glass fiber filter/probe rinse residues was performed as follows:

1. Fold the filter wearing clean plastic gloves and place it flat into the beaker containing the probe rinse residue.

2. Add enough 8 N Baker Ultrex® HNO_3 to completely immerse the filter.

3. Cover the beaker with a clean watch glass and gently reflux the contents over the heat for 6 hr.

4. Cool the beaker and contents.

5. Decant and filter the acid into a clean tared plastic bottle.

6. Add enough Milli-Q deionized water to rinse the watch glass, beaker walls, and filter material.

7. Filter the beaker contents through a precleaned No. 41 Whatman filter into the same plastic bottle containing the acid leaching medium.

8. Dilute the sample to achieve an acid composition of approximately 10% v/v HNO_3.

3.3.8.3 Process Waters: Process Waters were Prepared by EPA Method 4.1.3 Methods for Analysis of Water and Wastes vs. EPA 600/4-79-025--

1. Place 50.0 mL sample into a clean 250-mL beaker.

2. Add 3 mL HNO_3 (Ultrex®) (approximately 1 hr).

3. Evaporate to near dryness and then cool.

4. Add 3 mL HNO_3 (ULtrex®) and cover with a watch glass.

5. Reflux gently until clear.

6. Remove watch glass, evaporate to near dryness (approximately) and then cool.

7. Add 5 mL 8 N HNO_3 (Ultrex®) and heat gently.

8. Filter contents into a tared 30-mL plastic bottle (through a No. 41 Whatman paper).

9. Rinse beaker and watch glass with 10% (v/v) HNO_3 (Ultrex®) and fitler.

10. Continue rinsing sample glassware to obtain a final volume of 30 mL.

11. Record mass.

3.3.9 Preparation and Use of Internal and Surrogate Calibration Standards

Preparation and/or acquisition of accurate calibration standards is extremely crucial in achieving accurate quantification of sample components. It is also important that the calibration standards be prepared in the correct solvent, since the calibration standards are used for both direct analysis and for spiking. Compounds for calibration standards were obtained from commercial suppliers in the purest grade available.

3.3.9.1 Volatile Organic Compounds--

Volatile organic internal standard and surrogate calibration standards were:

1. Prepared in methanol.

2. Prepared from compounds of known, high purity.

3. Prepared in quantities of at least 10.0 mL and preferably 100.0 mL to minimize measurement errors.

4. Prepared at an original concentration of 1 to 10 mg/mL.

5. Transferred to Mininert valve top vials with no headspace for storage (only 5.0 mL of the original solution needs to be saved).

6. Stored at 4°C.

7. Prepared fresh on at least a monthly basis.

The volatile POHCs consist of liquids and gases. The liquid POHCs may be weighed into a 10-mL volumetric flask containing about 9.8 mL of methanol or added volumetrically from a syringe with the weight added determined from the volume and density of the compound.

The gases (chloromethane, bromomethane, chloroethane, and vinyl chloride) must be prepared gravimetrically in the hood using the following procedures:

- Attach a regulator with an on/off valve and a septum opening to the gas cylinder (preferably lecture bottle size).
- Open cylinder valve and regulator valve and allow a small amount of gas to escape.
- Fill a 5-mL valved gas-tight syringe with the gaseous POHC to the 5.0 mL mark.
- Lower the needle to 5 mm above the meniscus of about 9.8 mL of methanol contained in a 10.0 mL glass-stoppered volumetric flask. Slowly inject the gaseous POHC into the neck of the flask.
- Reweigh the flask, dilute to volume, stopper, and mix by inverting the flask several times.
- Calculate the concentration in milligrams per milliliter from the net gain in weight.

The volatile organic internal and surrogate calibration standards were used for spiking into water, for analysis as purge-trap-desorb calibration standards, spiking into samples for determination of recoveries, and flash vaporizing onto Tenax and Tenax/charcoal traps for analysis as calibration standards. The original stock solutions were diluted with methanol to provide calibration standards which cover at least a 100-fold concentration range, i.e., from 2 to 200 ng of each compound analyzed on-column.

3.3.9.2 Semivolatile Organic Compounds--

Semivolatile organic internal and surrogate calibration standards were:

1. Prepared in methylene chloride for analysis by GC/MS.

2. Also prepared in methanol, if soluble, for spiking into aqueous and waste feed samples. If the compounds were not soluble in methanol, the minimum required amount of methylene chloride or methylene chloride/toluene solution was used for spiking.

3. Prepared in quantities of at least 10.0 mL and preferably 100 mL to minimize measurement errors.

4. Prepared in concentrations of 1 to 10 mg/mL.

5. Stored at 4°C with the volumetric flask stopper wrapped with Teflon tape.

The semivolatile organic compounds consisted of liquids and solids. The liquid compounds were weighed or measured volumetrically as described for the volatile compounds. The solid POHCs were weighed and diluted to volume in a volumetric flask.

3.3.9.3 Metals--

Calibration standards for metal analysis by ICP and AAS was prepared from commercially available stock solutions obtained through the Alfa Division of the Ventron Corporation, from Fisher Scientific Company, or from Spex Industries. The calibration standards of the individual metals were prepared by transferring a known quantity of stock standard via calibrated auto-pipet into an acid-cleaned 100-mL volumetric flask. The volume was adjusted using 10% v/v Baker Ultrex® HNO_3 until the final volume of 100 mL was obtained. A standard blank was prepared by filling an acid-cleaned volumetric flask to the mark with the 10% v/v HNO_3 solution.

The final analyte concentration of the calibration standard was 10 µg/mL, except for potassium which was 100 µg/mL.

Standards of arsenic for AAS analysis were prepared by transfer of a known quantity of stock standard to an acid-washed 100-mL volumetric flask, using a calibrated pipet. The standard was diluted with 1% (v/v) HNO_3 (Ultrex®) until the mark was reached. Serial dilutions were made from this standard, using a calibrated pipet, to obtain a standard range of 0 to 200 ng/mL for arsenic.

3.3.10 <u>GC/MS Internal Quality Control</u>

Subsections 3.3.11 through 3.3.14 describe the specific GC/MS procedures that were used to analyze the different types of samples by GC/MS. Described below are the internal quality control procedures followed for all GC/MS analysis.

3.3.10.1 GC/MS Calibration and Analysis--

The daily GC/MS run routine included at least one calibration run at the beginning and end of the day. Additional calibration runs during the day were done if more than eight sample runs were made. Multilevel calibration standards were analyzed on a weekly basis.

The modified "Quality Control Protocol for the Fused Silica Capillary Column Gas Chromatography/Mass Spectrometry Determination of Semivolatile Organic Compounds"[2] was followed for analyses of semivolatile POHCs using FSCC.

3.3.10.2 Internal Standards--

All samples to be analyzed by GC/MS were spiked with internal standards just prior to GC/MS analysis. Waste feed extracts and aqueous samples to be analyzed for volatile POHCs were spiked with D_6-benzene at the 100 ng level.

Tenax traps for analysis of volatile POHCs from the volatile organic sampling train were spiked with D_6-benzene, perfluorobenzene, D_4-1,2-dichloroethane, and bromofluorobenzene at the 50 ng level. One milliliter aliquots of methylene chloride extracts of the waste feed samples, MM5 train samples and aqueous samples were spiked with 20 µg of D_{10}-anthracene internal standard by GC/MS facility personnel.

3.3.10.3 Surrogate Standards--

Surrogate standards are compounds added to the native sample matrix prior to sample extraction to determine if any sample matrix effects and extraction problems prevent good recovery of the surrogates from the sample. These compounds may give an indication of problems in recovering sample POHCs. The surrogate compounds used were decafluorobiphenyl, D_8-naphthalene, D_{12}-chrysene, in samples analyzed for semivolatiles and D_4-1,2-dichloroethane, and D_{10}-ethyl benzene in samples analyzed for volatiles (surrogates added at same time as internal standards for Tenax and Tenax/charcoal adsorbent traps).

3.3.10.4 Blanks--

Blanks are defined as system or process blanks and consist of all reagents used in sample preparation carried through the entire preparation process and finally analyzed by GC/MS. This activity assesses the purity of reagents and cleanliness of apparatus and environment. One or more system blanks were generated and analyzed with every batch of samples prepared or with every new batch of reagent material.

3.3.11 GC/MS Analysis of Waste Feed Samples for Volatile POHCs

The volatile POHCs in the tetragylme extract were analyzed by a purge-trap-desorb GC/MS method based on EPA Method 624[3] according to the procedures described below.

1. Calibrate the Finnigan-MAT CH-4 or Finnigan 4000 GC/MS instrument and ensure that EPA-specified tuning criteria are met for BFB and that m/z 84 for 100 ng of D_6-benzene yields about 100,000 area counts for analysis of a reagent water method blank.

2. Add 5.0 mL of reagent water to the purging device.

3. Spike the water with the internal standards (100 ng each).

4. Inject 10 µl of the tetraglyme extract of the waste into the water.

5. Purge sample with a flow rate of 30 ± 3 mL/min for 10.0 ± 0.1 min at ambient temperature.

6. At the end of the purge period, switch to the desorb mode so that the trapped organics are desorbed at 180°C with a flow rate of 30 mL/min.

7. Start the GC/MS analysis using the following conditions:

Detector: Mass spectrometer scanning from 40 to 260 amu
Column: 2 m x 2 mm ID, glass tube packed with 0.1% Carbowax 1500 on 60/80 mesh Carbopak C
Column temperature: 40°C (hold 3 min) to 175°C (15-min hold) at 8°C/min

8. After 4 min, switch from desorb mode to purge mode.

9. Replace purging chamber with clean purging chamber.

10. Purge and heat analytical trap to 200°C in preparation for next run.

11. Begin reverse search for the target POHCs and internal standards using the computer-automated reverse search routine or manual technique.

12. Inspect the quantification report from the reverse search to ensure that internal and surrogate standards were found and that the area counts are within ±30% of the value from the calibration standard.

Since the tetraglyme extract was not screened by GC/FID prior to GC/MS analysis, it is possible that the 10 µL of tetraglyme extract may not provide the optimum concentration for quantifying volatile POHCs in the sample. If several of the sample compounds saturated the GC/MS system during the GC/MS analysis, the sample should be reanalyzed using a smaller aliquot (or appropriately diluted aliquot) of the tetraglyme extract. Alternatively, if the concentration of the volatile POHCs in the sample was very low, the sample should be reanalyzed using a larger aliquot of the tetraglyme extract (up to 250 µL may be added to the 5.0 mL of reagent water).

3.3.12 GC/MS Analysis of Aqueous Samples for Volatile POHCs

The volatile POHCs in the aqueous samples were analyzed by a purge-trap-desorb GC/MS method (EPA Method 624[3]) according to the procedures described below.

1. Calibrate Finnigan-MAT CH-4 or Finnigan 4000 GC/MS instrument and ensure that EPA-specified tuning criteria are met for BFB and that m/z 84 for 100 ng of D_6-benzene yields about 100,000 area counts for analysis of a reagent water methanol blank.

2. Add 5.0 mL of the water sample from a full 40-mL VOA vial to the purging device.

3. Spike the water with the surrogate standards and internal standards (100 ng each).

4. Purge sample with a flow rate of 30 ± 3 mL/min for 10.0 ± 0.1 min at ambient temperature.

5. At the end of the purge period, switch to the desorb mode so that the trapped organics are desorbed at 180°C with a flow rate of 30 mL/min.

6. Start the GC/MS analysis using the following conditions:

Detector: Mass spectrometer scanning from 40 to 260 amu
Column: 2 m x 2 mm ID, glass tube packed with 0.1% Carbowax 1500 on 60/80 mesh Carbopak C
Column temperature: 40°C (hold 3 min) to 175°C (15-min hold) at 8°C/min

7. After 4 min, switch from desorb mode to purge mode.

8. Replace purging chamber with clean purging chamber.

9. Purge and heat trap to 200°C in preparation for next run.

10. Begin reverse search for the target POHCs and internal standards using the computer-automated reverse search routine or manual technique.

11. Inspect the quantification report from the reverse search to ensure that internal standards were found and that the area counts were within ±30% of the values for the calibration standard.

In the unlikely event that any of the volatile POHCs saturated the GC/MS system during analysis of the aqueous samples, an aliquot of the water sample may be diluted with reagent water (e.g., dilute 1.0 mL of water sample to 5.0 mL with reagent water) and reanalyzed by purge-trap-desorb GC/MS.

3.3.13 Analysis of Tenax and Tenax/Charcoal Adsorbent Traps for Volatiles

The volatiles in the adsorbent tubes were analyzed according to a modified purge-trap-desorb GC/MS procedure. The traps were first spiked with internal standards and the contents of the traps thermally desorbed into the purge-trap-desorb system using a Nutech Thermal Desorption apparatus.

3.3.13.1 Sample Spiking by Flash Vaporization--

1. Remove a preconditioned (heated at 250°C with 30 mL/min helium flow for 2 hr) adsorbent trap from a screw-cap vial and insert into a 1.0 in. Swagelock nut fitting connected to a GC injection port. Be sure flow of helium gas is off, but that flow is about 30 mL/min when the gas is turned on and an adsorbent trap is in place. Only handle the sample adsorbent tubes with tweezers and/or with clean cotton gloves.

2. Turn gas on and, using the solvent flush technique, inject 1.0 µL of a methanolic calibration standard containing 50 ng/µL of D_4-1,2-dichloroethane, perfluorobenzene (hexafluorobenzene) (PFB), 4-bromofluorobenzene (BFB), and D_6-benzene.

3. After inserting needle into the GC septa, wait 15 sec, shut off gas flow using shut-off valve, and remove the syringe needle.

4. Remove adsorbent trap from GC injection port, return to screw-cap vial, and submit for GC/MS analysis.

5. Prepare calibration standards by spiking additional adsorbent traps with separate methanolic solutions containing the POHCs at the desired levels and the internal standards at the 50 ng level.

6. No more than a total of 2 µl of methanol should be injected into the traps. To prepare calibration standards with multiple levels of POHCs, prepare the corresponding methanolic solutions. For example, to spike an adsorbent trap with 50 ng of each POHC, prepare a 50-ng/µL solution of the POHCs in methanol.

3.3.13.2 GC/MS Analysis of Adsorbent Traps--

1. Prepare the purge-trap-desorb and GC/MS system for analysis of trap:

- Turn 6-port valve to "purge" mode.
- Cool purge-trap-desorb analytical trap to ambient temperature.
- Ensure flow rate of helium through Nutech desorption unit and purge tower is 40 mL/min.

2. Insert adsorbent trap into the Nutech desorption unit. Immediately close Nutech lid and start stopwatch.

3. Enter the data acquisition information in the GC/MS data system.

4. At the end of 10.0 min, immediately:

- Switch purge-trap-desorb 6-port valve to the "desorb" mode.
- Heat the purge-trap-desorb analytical trap to 180°C.
- Start the GC program (40°C for 3 min, then temperature program to 175°C at 8°C/min).
- Start the GC/MS data acquisition. (The data acquisition should continue for 700 scans or about 20 min. The GC oven should also be set to cool to 40°C at the end of the acquisition.)

At the end of the GC/MS run:

- Turn off heat to the purge-trap-desorb analytical column.
- Switch 6-port valve back to the "purge" mode.

The purge-trap-desorb GC/MS system is now ready to analyze another adsorbent tube sample.

3.3.14 <u>GC/MS Analysis of Methylene Chloride Extracts</u>

3.3.14.1 POHC Analysis--

The methylene chloride extracts were analyzed by GC/MS on a fused silica capillary column according to a modified version of EPA Method 625[1] as described below.

1. Tune and calibrate the GC/MS instrument so that EPA-specified tuning criteria are met for DFTPP at the 50 ng level and so that 20 ng of D_{10}-anthracene yields about 130,000 area counts for m/z 188.

2. Spike the 1.0 mL of sample with 20 μg of D_{10}-anthracene internal standard such that the final concentration is 20 ng/μL.

3. Analyze the sample by GC/MS using the following conditions:

Sample volume: 1 to 2 μL
Column: 15 m or 30 m x 0.25 mm ID fused silica capillary column coated with SE-52 methyl silicone (or equivalent, e.g., DB-5)
Column temperature: 40°C (4-min hold), then 10°C/min to 325°C (10-min hold)
Column flow: 45 cm/sec linear velocity (He)
Injection temperature: 280°C
Transfer line temperature: 300°C
Injection: Grob-type, splitless with 45-sec split time
Scan range: 40 to 475 amu
Scan rate: 0.75 to 1.0 sec/scan

3.3.14.2 Analysis of PCDDs and PCDFs--

One stack effluent sample from each of the plants was analyzed for tetra- and penta-chlorinated dibenzodioxins and dibenzofurans. Since interferences are often observed during analysis of complex extracts for PCDDs and PCDFs by GC/MS, it was necessary to purify portions of the extracts using the method of Hanlers et al.[5] described below.

Generally, one-half (500 μL out of 1.0 mL extract) of the total of the combined train effluent samples was used for cleanup. First, the extract was diluted to 60 mL with hexane and washed with 25 mL of 1 N KOH solution followed by four 50-mL portions of concentrated sulfuric acid. The hexane was then washed with a 25-mL portion of water, and the water and hexane layers were neutralized by the addition of powdered sodium carbonate. The aqueous layer was discarded, and the hexane dried by passage through a 11 mm ID x 500 mm glass column containing 10 cm of anhydrous powdered sodium carbonate. The hexane was collected in a K-D concentrator tube and concentrated to 3 mL for cleanup on an alumina chromatographic column.

The alumina columns were prepared by packing 4.5 cm of neutral alumina into a disposable pipet. The alumina was topped with 0.5 cm of anhydrous granular sodium sulfate. The column was washed with 4 mL of methylene chloride and stored in an oven for 72 hr at 225°C. The columns were then equilibrated to room temperature prior to use by transferring them to a desiccator over Drierite.

The alumina column was prewetted with 1 mL of hexane, and then the 3 mL of hexane concentrate was transferred to the column. The column was eluted with 6 mL of carbon tetrachloride (which was not analyzed) followed by 4 mL of methylene chloride which was collected and evaporated just to dryness. Two separate 2-mL portions of hexane were added and evaporated just to dryness. The residue was dissolved in 3 mL of hexane and chromatographed on a

second slumina column using exactly the same procedures described above. The methylene chloride eluate from the second column was evaporated just to dryness and taken up in the 2 mL of hexane which was concentrated to a volume of about 50 μL for analysis by selected ion monitoring using fused capillary gas chromatography/mass spectrometry (HRGC/LRMS-SIM) for PCDDs and PCDFs. The ions which were used for monitoring are listed in Table B-4.

TABLE B-4. GC/MS-SIM IONS

No. of chlorines	Biphenyls	Dibenzofurans	Dibenzo-p-dioxins
1	188/196[a]	202/204	218/220
2	222/228	236/238	252/254
3	256/262	270/272	286/288
4	289/308	304/306	320/322[b]
5	322/330	338/340	354/356
6	358/364	372/374	388/390
7	390/398	408/410	424/426
8	426/446[a]	442/444	458/460
9	460/466	-	-
10	492/510	-	-

[a] Includes ions for surrogate and/or internal standard.

[b] For HRGC/LRMS-SIM ions 319.8967, 321.8937 were monitored.

The sample extracts were generally analyzed by high resolution fused silica capillary column, gas chromatography/mass spectrometry HRGC/LRMS-SIM for penta- and tetra-chlorinated dibenzodioxins and furans. Samples which gave a positive response for tetrachlorodibenzodioxin (TCDD) were reanalyzed by GC/MS on a special glass capillary column coated with the liquid phase SP-2330 (phenyl cyanopropyl silicone) available from Supelco and with high resolution mass spectrometry detection. The SP-2330 column is capable of separating the 2,3,7,8-TCDD isomer from the other TCDD isomers while the high resolution mass spectrometer provides confirmation that a given compound has the correct mass to be a TCDD.

3.3.15 GC/MS Data Retrieval

Generally, the information required from the GC/MS data resulting from each of the analyses described above was the amount of each POHC of interest. However, for some samples information on the identify and approximate amount of other sample components was also needed. The information was obtained according to the following procedures.

1. The raw GC/MS data were searched for the target POHCs using a computer-automated reverse search routine, or by manual search.

2. The quantification report from the reverse search was visually inspected to ensure that internal standards were found by the search routine and that the area counts are ±30% of the values from the calibration standards. Manual confirmation of some of the computer search results was often required.

3. The amounts of the target compounds found in the extract were corrected to sample concentrations using:

$$\text{concentration, } \mu g/g \text{ or } \mu g/L = \frac{\mu g \text{ of Internal Standard}}{\text{gram or liter of sample}} \times \frac{A_s}{A_{is}} \times \frac{1}{RF}$$

where: A_s = Area of the primary characteristic ion of the compound being quantified.

A_{is} = Area of the primary characteristic ion of the internal standard.

RF = Response factor of the compound being quantified.

4. The mass spectra of major peaks in the sample, which were not target compounds, were searched against the National Bureau of Standards (NBS) library.

5. The results of the NBS library search results were examined manually to determine if they provided a reasonable identification for the compounds. Additional manual interpretation of the mass spectra was applied when needed.

6. Quantification of nontarget compounds were estimated based on the area counts from the total ionization of the mass spectrum compared to the total ionization area counts of the internal standard.

3.3.16 Analysis of Metals

3.3.16.1 ICP Analysis--

1. Generate a calibration curve using the prepared ICP standards and enter curve into computer.

2. Aspirate the sample into the argon plasma and allow sample to equilibrate.

3. Begin instrumental analysis and obtain three readings of 10-sec duration.

4. Rinse the nebulizer with deionized water to purge the lines of traces of the previous sample.

The average value of the three readings was printed out in hard copy and stored on magnetic disk by the computer.

3.3.16.2 AAS Analysis--

Atomic absorption spectroscopy was used to analyze for the volatile metal arsenic according to the procedures described below.

1. Set up Perkin-Elmer 306 atomic absorption spectrometer and HGA 2100 furnace according to the manufacturer's guidelines.

2. Generate a calibration curve using the prepared standard solutions by injecting 25 μL of the solution into the furnace.

3. Inject 25 μL of sample for analysis.

3.3.17 Extraction Procedure (EP) Toxicity Testing

Selected kiln ash samples were analyzed for Extraction Procedure (EP) toxicity according to the guidelines specified in the Federal Register, May 19, 1980, p. 33121-33133.[4] The maximum concentrations of the selected contaminants are shown in Table B-5.

The kiln ash samples (100 g of solid material) were leached for 24 hr with distilled water in a special leaching device which stirs the sample. The pH of the leachate was checked at approximately 1-hr intervals during the day and adjusted to 5.0 with 0.5 N acetic acid. The leachate was then separated from the ash using filtration through a 0.45 μm membrane filter. The leachate was then analyzed for the species shown in Table B-5. The analytical procedures are described below.

3.3.17.1 Analysis for Organic (Chlorinated Pesticides and Phenoxy Herbicides)--

The chlorinated pesticides were analyzed according to standard EPA methods as described below.

3.3.17.1.1 Sample extraction--Separate aliquots of the leachate sample (at least 250 mL and preferably 1 L) were analyzed for the chlorinated pesticides and phenoxy herbicides. The chlorinated pesticides were extracted three times with 60-mL aliquots of 15% (v/v) methylene chloride in hexane. The extracts were combined, dried through a short column of anhydrous sodium sulfate and concentrated to 10 mL using K-D evaporation.

The leachate sample for analysis of the chlorinated phenoxy herbicides was first acidified to pH 2 with concentrated sulfuric acid and extracted with a 150-mL aliquot and two 50-mL aliquots of diethyl ether.

3.3.17.1.2 Analysis of chlorinated pesticides--The hexane extract (10-mL) was analyzed directly for the four chlorinated pesticides by injecting 1-μL aliquots directly onto a gas chromatograph (GC) equipped with an electron capture detector (ECD) and operated at the following conditions:

TABLE B-5. MAXIMUM CONCENTRATION OF CONTAMINANTS FOR CHARACTERISTIC OF EP TOXICITY[a]

EPA hazardous waste number	Contaminant	Maximum concentration (mg/L)
D004	Arsenic	5.0
D005	Barium	100.0
D006	Cadmium	1.0
D007	Chromium	5.0
D008	Lead	5.0
D009	Mercury	0.2
D010	Selenium	1.0
D011	Silver	5.0
D012	Endrin (1,2,3,4,10-10-hexachloro-1,7-epoxy-1,4,4a,5,6,7,8a-octahydro-1,4-endo, endo-5,8-dimethano naphthalene)	0.02
D013	Lindane (1,2,3,4,5,6-hexachloro-cyclohexane, gamma isomer)	0.4
D014	Methoxychlor (1,1,1-trichloro-2,2-bis [p-methoxyphenyl]ethane)	10.0
D015	Toxaphene ($C_{10}H_{10}Cl_8$, technical chlorinated camphene, 67-69% chlorine	0.5
D016	2,4-D (2,4-dichlorophenoxyacetic acid)	10.0
D017	2,4,5-TP Silvex (2,4,5-trichloro-phenoxypropionic acid)	1.0

[a] Federal Register, May 19, 1980, p. 33122.

Column: 1.8 x x 2 mm ID glass column packed with 1.5% SP-2250/1.95% WP-2401 on 100/120 mesh Supelcoport
Flow: He at 30 mL/min
Injector temperature: 250°C
Detector temperature: 300°C
Column temperature: 180°C isothermal

Individual calibration solutions of each of the four pesticides were also prepared at three different concentration levels and analyzed along with the sample extracts.

3.3.17.1.3 Analysis of phenoxy herbicides--The phenoxy herbicide acids were derivatized to their methyl esters according to EPA Method 615, prior to analysis by GC/ECD. The diethyl ether extract was added to a K-D flask containing 15 mL of reagent water and 2 mL of 37% (w/v) aqueous potassium hydroxide. The solution was heated at about 65°C for 60 min to ensure that the phenoxy herbicides were converted to their potassium salt form. The solution was then transferred to a 60-mL separatory funnel, and the impurities were removed using two extractions with cyclohexane (the herbicides remain in the aqueous phase). The hexane washes were discarded. The aqueous solution was then acidified with 2 mL of cold (4°C) 25% H_2SO_4 in order to convert the herbicide salts to the acid form. The acids were then extracted into methylene chloride. The methylene chloride extract was dried with anhydrous sodium sulfate, allowed to stand for 2 hr, concentrated to 6 to 10-mL using K-D evaporation, solvent exchanged into toluene with the addition of 0.5 mL of toluene, and concentrated to a volume of 0.4 mL.

The toluene extract was esterified using boron trifluoride. First, 0.5 mL of BF_3/methanol reagent was added to the extract, and the sample heated for 30 min on a 50°C hot water bath. The solution was cooled, and about 5 mL of a neutral 5% aqueous sodium sulfate solution was added. The solvent phase was separated from the aqueous sodium sulfate phase and added to the top of a small column prepared by plugging a disposable pipet with glass wool and packing it with 2.0 cm of anhydrous sodium sulfate over 1.5 cm of Florisil adsorbent. As the eluate was collected in a graduated tube, additional small quantities of toluene were passed through the column until a final volume of 5.0 mL of eluate was obtained.

The samples were analyzed by GC-ECD along with calibration standards which were derivatized using the same procedure as for the samples.

3.3.17.2 Analysis for Metals--
The samples were analyzed for the metals listed below by the U.S.EPA wastewater spectroscopic methods[4] indicated below:

Metal	Method
Arsenic	206.3 hydride generation atomic absorption
Barium	208.1 flame atomic absorption
Cadmium	213.1 flame atomic absorption
Chromium	218.1 flame atomic absorption
Lead	239.1 flame atomic absorption
Mercury	345.1 cold vapor atomic absorption
Selenium	270.3 hydride generation atomic absorption
Silver	272.1 flame atomic absorption

As prescribed by the regulations, all samples were analyzed by a three point method of standard additions procedure to compensate for potential matrix interference effects.

3.4 DATA REDUCTION, VALIDATION, REPORTING, AND DOCUMENTATION

The most important analytical data resulting from this program were the amounts of the POHC analytes in each of the samples so that correct DRE calculations could be made to evaluate the performance of the tested incinerators. It is very important to know the error that may be associated with each of the measurements and thus with the DRE determinations so that the information is used correctly in regulatory decisions.

Most of the data for this program were outputted using a computer, i.e., the ICP data and the GC/MS data. The data reduction techniques used for these instruments are discussed below.

3.4.1 POHC Data

3.4.1.1 GC/MS Data Reduction--

The quantification of most sample components was based on the internal standard method in which a constant amount of the internal standard was added to all samples, blanks, and calibration standards just prior to analysis.

The raw data for the quantification of the sample components consisted of the computer-measure peak areas of the characteristic mass fragmentation ions of the internal and surrogate standards and the POHC analytes of interest. Most commonly the raw data were converted to concentrations by using mass spectrometric response factors relative to the internal standard. Ideally the response factors were constant over the entire concentration range of interest. However, the response factors may vary with concentration. For these cases the response factor (RF) was plotted against the concentration of the analytes in the calibration standards, using a minimum of three concentrations over the range of interest. The response factors were calculated according to the equation:

$$RF = \frac{(As)(Cis)}{(Ais)(C_s)}$$

where: As = Area of primary characteristic ion of the compound being quantified.

Cis = Concentration or amount of the internal standard.

Ais = Area of the primary characteristic ion of the internal standard.

C_s = Concentration or amount of the POHC in the calibration standard.

Following sample analysis, the appropriate response factor was taken from the calibration curve (or the constant response factor was used) and the concentration of the compound in the sample was calculated according to the equation:

$$\text{POHC concentration} = \frac{(As)(Cis)}{(Ais)(RF)}$$

It is very important to determine the correct value for Cis, the concentration of the internal standard relative to the original sample matrix. For example, if a 5-g sample of hazardous waste is dispersed into 150 mL of methylene chloride and 1 mL of the extract is spiked with 20 μg of D_{10}-anthracene prior to GC/MS analysis for semivolatile POHCs, the concentration of the internal standard is calculated according to the following:

$$\frac{150\ \text{mL}}{5\ \text{g}} \times \frac{20\ \mu\text{g}}{\text{mL}} = \frac{600\ \mu\text{g}}{\text{g}}$$

Therefore, 600 μg/g would be used for Cis in determining the concentration of the POHC in the waste feed sample.

In the combined MM5 train extracts, the total amount, i.e., μg, of a POHC found in the samples was determined rather than a concentration. These data were then provided to the Engineering Support Staff who calculated the concentrations of the components in the stack based on the volume of dry stack gas samples.

All GC/MS quantification values were rounded off to two significant figures.

3.4.1.2 GC/MS Data Validation--

The principal criteria that were used to validate the integrity of the GC/MS data acquired and reported during this program were the following.

1. Verification on a frequent basis by the analytical task leader that all raw data generated in the preceding week were stored on magnetic tape and/or in hard copy and that storage locations were documented in the laboratory chain-of-custody records.

2. Examination of at least 5% of the raw data (e.g., chromatograms) on a frequent gasis by the analytical task leader to verify adequacy of documentation, confirm peak shape and resolution, assure that the computer was sensing peaks appropriately, etc.

3. Confirmation that raw areas for internal standards and calibration standards and raw and relative areas for surrogate compounds were within 50% of the expected value.

4. Reporting of all associated blank, standard, and QC data along with results for analyses of each batch of samples.

5. Reporting of all analytical data for samples with no values rejected as outliers, because of the small number of replicate samples for analysis.

3.4.1.3 GC/MS Data Reporting--

Two types of GC/MS data reporting formats were required for this program:

- Amount and/or concentration of specific POHCs in a given sample.
- Identities and estimated amounts of major sample components in the waste samples.

When only the results of the POHC analyses were of interest in a set of samples, the results were reported to the Engineering Support Staff in simple tables. The units varied with the type of sample. For example a waste feed concentration was reported in μg/g, a MM5 combined extract was reported in total μg, and a scrubber effluent extract was reported as μg/L.

3.4.2 Metals Data

3.4.2.1 Data Reduction--

3.4.2.1.1 ICP data reduction--Sample analyte concentrations were generated on the ICP emission spectrometer by the Jarrell-Ash Sample Analysis Task (SAT) computer program. SAT measures intensities counts on each of the 30 detection channels, compares the counts to a linear intensity count versus concentration relationship stored in the computer during instrument calibration. Multiplication by dilution factors, etc., were also done at this time. Immediately following analysis of a sample, the final sample concentrations were both printed on the computer terminal and stored on disk for quality control and report writing by other computer programs.

3.4.2.1.2 AAS data reduction--Sample analyte concentrations were generated on the Perkin-Elmer 306 atomic absorption spectrophotometer by first measuring the absorbance of a sample. Then this absorbance was converted to a digest analyte concentration by comparing the absorbance to an absorbance versus concentration calibration curve. This comparison was performed on a Hewlett-Packard 9815A programmable calculator. Dilution factors were

applied by hand calculation to the digest concentrations to arrive at the final sample analyte concentrations.

3.4.2.2 ICP Data Validation--

3.4.2.2.1 Instrument validation--

- The occurrence of spectral interferences in ICP source emission spectrometry is not as frequent as with other emission sources but is common enough to require corrective measures. The common types of spectral interferences experienced in ICP-AES are: (a) direct overlap by an interfering emission peak; and (b) baseline shifts due to stray light and molecular emission. These interferences both result in falsely high analyte emission and, hence, analyte concentration determinations.

- Interferences were identified for a new sample matrix by aspirating a representative sample and performing 63, 2-sec emission integration counts in a scan 1 Angstrom on either side of each analyte emission peak centerline.

- On-peak interelement correction was used to remove the effects of interferences by subtracting a concentration amount from the interfered element detection channel. The amount to be subtracted equaled (concentration of interfering element) x correction factor. The correction factors were determined by measuring the false positive reading on the interfered channel when a sample containing 10 ppm interfering element was measured. The correction factor equals the false positive concentration per 1 ppm interfering element. Correction factors were then placed in Group 4 of the appropriate Analytical Control Table (ACT). Correction factors are specific for a given sample matrix and observation position in the inductively coupled plasma.

- All analysis data used to generate correction factors and copies of each Group 4 data were placed in the program "Spectral Interferences" Technical Record Book.

- Correction factors were redetermined each time the ICP torch was cleaned and reassembled.

- Correction factors were also redetermined each time repeated analysis of the Interference Check Standard did not give results within ±10% of the true values.

- A representative sample from each sample preparation batch was spectrum scanned, plotted, and evaluated to confirm that all spectral interferences were being compensated by correction factors.

3.4.2.2.2 Accuracy verification of instrument calibration standards--

- New calibration standards were prepared every 30 days.

- Each type of sample matrix used a separate set of calibration standards.

- Each volumetric flask holding the calibration standards was labeled with the standard name, ACT name, and date.

- The accuracy of each new batch of calibration standard was verified by analyzing a matrix-matched U.S.EPA analytical quality control (AQC) standard. Accuracy was measured by calibrating the ICP spectrometer with the new standards and analyzing the AQC standard five times. Accuracy was acceptable if all measured values for the AQC standards were within ±5% of the certified values. If verification was not successful, the spectrometer was recalibrated and the test repeated. If verification was still not successful, new standards were prepared.

- All terminal output for the verification test was placed into the program LRB.

3.4.2.2.3 Verification of daily instrument calibration--

- Two quality control standards were used to verify the accuracy of the initial calibration of the ICP emission spectrometer and to monitor instrument drift. These standards were:

  ICS - Instrument Check Standard
  STD1 - Calibration reagent blank

- ICSs were prepared monthly or as needed by the trace metal analysis leader.

- The true or accepted concentration values for a new ICS were determined by first successfully calibrating the ICP spectrometer with existing quality control samples and performing 20 replicate analyses of the new ICS. The mean standard deviation, and percent relative standard deviation for the replicate analyses were determined (TDTP).

- The true or accepted values for STD1 were determined the same way.

- All computer terminal printouts were placed in the program "Blank Instrument Check Standard" Technical Record Book.

- As described in Section 3, "Daily Instrument Calibration Procedure,"STD1 and ICS were analyzed at the beginning and every 10th analysis for a sample set to assure continued acceptable instrument calibration. The control limits were:

STD1 ± standard deviations for mean concentration values

ICS ± 5% from true or accepted concentration values

- Any samples analyzed after the last successful verification of the daily instrument calibration were reanalyzed after calibration.

3.4.2.3 Metals Data Reporting--

Separate data reporting forms were used to report ICP and AAS data to the analytical task leader.

3.4.2.3.1 ICP data reports--The ICP data reporting forms were generated by the computer. The concentration units are given in the first line of the report. For compounds not detected, a 'less than' value was reported which is the detection limit for that element based on the results of the analysis of the calibration standards.

The ICP computer also generated additional data outputs on separate report forms including:

- Percent relative standard deviation (RSD) between duplicate samples.
- Accuracy achieved for fortified samples.
- Percent RSD between duplicate calibration standards.

3.4.2.3.2 AAS data reports--The AAS analysis data reports were completed manually. Each form has space for the analysis of a single element in several samples, e.g., all the samples analyzed for a given metal at a trial burn.

3.4.3 Documentation Procedures

A tremendous quantity of data and information was generated during the conduct of the analytical aspects of this program, all of which was archived. The analytical task leader is responsible for directing the archiving of the sample information including the following:

- Dates and condition of sample receipt.
- Storage location of samples and extracts.
- Date of sample extraction, workup, and analysis.
- Sample numbering and identification scheme.
- Dates of GC/MS analyses.
- All volumes and weights used.
- Dilution and concentration factors.
- Amounts of internal standards used.

- Internal standard area responses.
- Injection volumes.
- Relative response factors used for quantification.
- Scan number and retention time of GC/MS peaks.
- Most intense mass spectral fragmentations.
- Absolute and/or relative retention times.
- Compound identifications.
- Total ion chromatograms.
- Library search results.
- 9-Track tape storage files of all GC/MS data.
- Results of analysis of calibration standards.
- Mass spectrometer tuning results.
- Instrument maintenance records.

Most of the data and information was taken from the computer hard-copied output, from the LRBs and from total ion chromatograms. In most cases, the recording of the data and information was straightforward. Some of the specific details of the documentation procedures are discussed below.

- One program LRB was used to record all sample receipt, logging, storage, and sample routing information.
- All samples and sample extracts were carefully labeled with a unique number traceable to the log-in LRB.
- One program LRB was used for the trial burns to record all information pertaining to sample extraction, screening, and preparation for GC/MS analysis.
- Solvent and chemical lot numbers were recorded in the experimental LRBs.
- The details of the GC/MS analyses were recorded in notebooks assigned to each GC/MS instrument.
- GC/MS data were taped at regular intervals (i.e., weekly) to provide a backup to the data on disk and for permanent storage of the data at the end of the project.
- All GC/FID chromatograms from sample screening studies were placed into file folders, labeled with sample number and project number, and stored with the analytical task leader at the end of the project.

- All GC/MS computer output was placed into file folders labeled with sample number and project number and stored with the analytical task leader at the end of the project.

- All project LRBs were archived at the end of the project.

- The GC/MS notebooks were controlled by the GC/MS facility manager.

3.4.4 GC/MS Data Storage

All computer generated mass spectrometry data were transferred from the original storage medium (hard disk drives) to 2,400 ft magnetic tape for permanent storage. All magnetic tapes are stored in a locked lab for security reasons. The organization of the data files stored on magnetic tape include: (a) identifying number on each magnetic tape recorded in chronological order; and (b) all file names archived are recorded into hardbound magnetic tape lab books and an Apple II microcomputer. Entries into the hardbound books include information regarding magnetic tape number and a block number (up to four disks full of data can be stored on a magnetic tape) indicating location of data on a magnetic tape. The transfer of similar information on the microcomputer allows for quick searching of magnetic tape location and other searchable variables such as project number, date of analysis, and instrument used for analysis.

3.5 PREVENTIVE MAINTENANCE

3.5.1 Mass Spectrometry Facility

The Mass Spectrometry Facility houses three GC/MS systems, all of which were used on this program. A regular maintenance program for the mass spectrometry laboratory was practiced to assure the proper operation of all equipment. The preventive maintenance program consisted of both scheduled (preventive maintenance) and nonscheduled maintenance procedures. All maintenance procedures performed on the instruments were recorded in the LRB assigned to each instrument. In addition, any instrument repair not performed by the laboratory personnel was handled by the electronic support service group which also adheres to a record keeping program.

The scheduled maintenance involved the service performance of the instruments at regular intervals and covered such activities as the following:

- Clean ion source.
- Change pump oil.
- Add calibration compounds to reservoir.
- Clean and adjust computer disk heads.
- Change GC septa.
- Change filters in the computer disk drives.
- Change the filters in the cooling water lines.

The nonscheduled maintenance program involved the necessary servicing of equipment on an "as needed" basis. This can include items in the scheduled maintenance program but most often involves these types of services:

- Check or replace ferrules and tighten transfer line nuts.
- Replace gaskets.
- Clean or replace the jet separator.
- Replace thermistors and fuses.
- Clean the ion source following unexpected "dirty" samples.
- Replace filament.

3.5.2 Metals Analysis Facility

The metals analysis facility consists of the Jarrell-Ash Atom Comp Series 155 ICP atomic emission spectrometer and three atomic absorption spectrometers, a Varian AA-6DB, Varian AA6, and Perkin-Elmer 306, all equipped with background correction and digital readout.

3.5.2.1 ICP--

1. The daily scheduled maintenance for the ICP included:

- Check tip of torch for any buildup of salt or particulate matter. The torch can be cleaned with very dilute nitric acid or warm water if necessary. After cleaning, reposition the torch as directed in the Jarrell-Ash manual.

- Examine the spray chamber. The atomized solution should create a very dense fog in the chamber which should not have a fixed flow direction. Adjustment of the nebulizer may be necessary if the spray appears erratic or misdirected.

- Check the peristaltic pump delivery rate. The ideal value is 1.8 mL/min for the fixed crossflow nebulizer and 3.2 mL/min for the high solids nebulizer.

- At the completion of a day's operation, aspirate distilled water through the system for 5 min as a rinse.

2. The monthly scheduled maintenance for the ICP included:

- Clean the torch assembly by immersion in 8 N HNO_3. Realignment of the torch and observation zone positioning will also be necessary.

- Check the gas and coolant water lines for leaks.

- Perform a detection limit check as outlined in the Operator's manual.

3. The nonscheduled maintenance for the ICP included:

- Check and realign the quartz torch.
- Check and realign the exit slits for some of the channels to optimize the signal-to-noise characteristics.

3.5.2.2 Perkin-Elmer 306 Spectrophotometer--

3.5.2.2.1 Daily maintenance--

- Inspect EDL source for damage.
- Inspect spectranetor "physically" for damage.
- Pressure check cooling water lines to furnace.
- Inspect and replace furnace electrodes, if necessary.
- Pressure check Argon gas line.
- Wipe clean furnace head.
- Inspect and replace graphite tube, if necessary.

3.5.2.2.2 Monthly maintenance--

- Inspect all electrical connections and repair as necessary.
- Clean accessible lenses, gas, and water and windows with ethanol and a lens cloth.

3.5.2.2.3 Nonscheduled maintenance--

- Replacement of EDL source.
- Periodic adjustment of the D_2 background correction.

3.6 REFERENCES

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